VOL. XL 1921

# TRANSACTIONS

OF THE

# AMERICAN ELECTROCHEMICAL SOCIETY.

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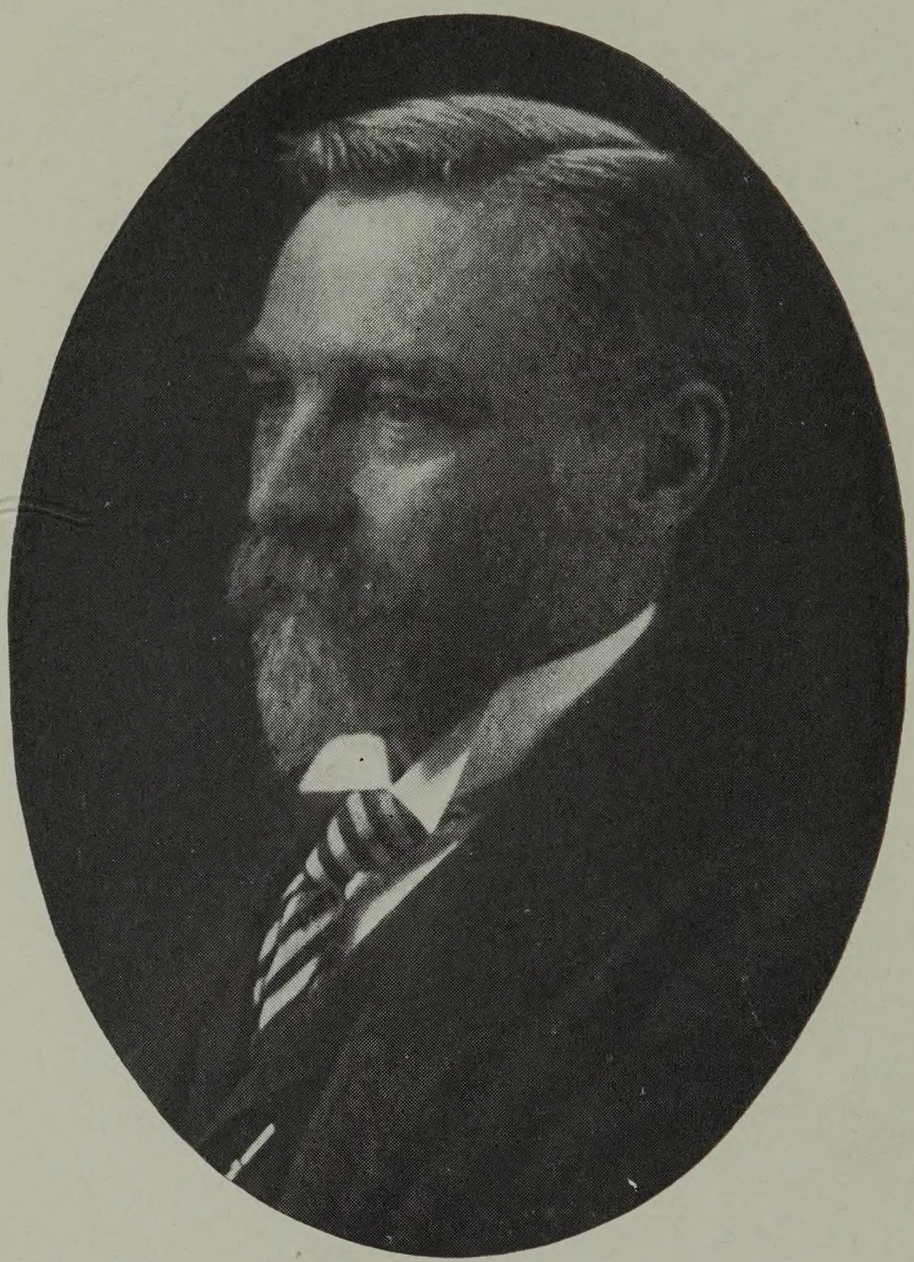

JOSEPH W. RICHARDS

PRESIDENT OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

1902 TO 1904

SECRETARY, 1907 TO 1922

BORN, JULY 28, 1864 DIED, OCTOBER, 12, 1921

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## VOLUME XL

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## FORTIETH GENERAL MEETING

LAKE PLACID CLUB, N. Y.

SEPTEMBER 29, 30 AND OCTOBER 1, 1921

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VOLUME XL 1921

# TRANSACTIONS

OF THE

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## PROCEEDINGS

CONDENSED MINUTES AND RECORD OF THE FORTIETH GENERAL MEETING OF THE SOCIETY, HELD AT THE LAKE PLACID CLUB, N. Y., SEPTEMBER 29, 30 AND OCTOBER 1, 1921

There were 65 members and 48 guests, or a total of 113, registered at this meeting.

### PROCEEDINGS OF THURSDAY, SEPTEMBER 29

President Acheson Smith called the meeting to order at 9.30 A. M. in the Music Room of the Lakeside Clubhouse, Lake Placid Club. After a few words of introduction he presented Dr. Melvil Dewey, president of the Lake Placid Club, for many years secretary of the Board of Regents of New York State and author of the Dewey Decimal System. Dr. Dewey heartily welcomed the members and particularly mentioned the most interesting spots in the Adirondacks which members should visit during their stay at the Club.

Papers by the following were then presented for discussion: Charles Vickers; W. A. Cowan, L. D. Simpkins and G. O. Hiers; Colin G. Fink and C. H. Eldridge, J. Newton Friend, C. J. Rodman, Raymond Freas, Alexander Lowy and E. H. Haux, N. Kameyama, P. C. Alsgaard, H. M. Goodwin and E. C. Walker, B. G. Worth. These papers are printed in full in these Transactions. Dr. J. W. Richards also related some interesting recent electrometallurgical developments in Scandinavia, which are embodied in these Proceedings.

At noon the directors of the Society met at dinner for the

purpose of discussing Society affairs; the meeting was continued at luncheon on Saturday.

Thursday afternoon was given over entirely to social events. A party of about 45 in number took the motorboat ride around Lake Placid, which with its irregular shore line and its several islands, made the trip most picturesque; the magnificent autumnal shades of the trees on the mountain slopes and the exhilarating air were great inspirations. Golf was one of the sports which found favor in the eyes of many, and to which the magnificent courses of the Club afforded splendid opportunities.

At 8 P. M. members and guests gathered in the auditorium of the Forest Clubhouse, where Dr. Dewey outlined briefly the objects and ideals of the Lake Placid Club, its history and wonderful achievements. Immediately afterwards an unusually interesting and most fascinating address on "Chemistry and the Stars" was delivered by Professor Harlow Shapley, of the Harvard Observatory. The address was illustrated with numerous photographs taken with the largest telescope in the world, that of Mt. Wilson observatory. Remarkable photographs of star clusters, nebulæ and nebulosity, star spectra; photographs of the sun, moon and Jupiter; of the interior of the Mt. Wilson Observatory, "one of the largest engineering efforts in pure science, and the largest investment ever made devoted entirely to idealism, and one that has been entirely successful."

The star spectrum photographs demonstrated that "in the sun the temperature is high enough to dissociate titanium oxide into its elements; in still hotter suns, titanium itself is 'crippled,' *i. e.*, one of the electrons has been thrown off and this fact is revealed in the spectrum." The spectrum of a region of the great Orion nebula clearly revealed the bright lines due to incandescent "nebulium, hydrogen, nitrogen, carbon, helium and others." "We do not know what nebulium is, but we know something of its properties. What may be the reward when we solve the mystery of nebulium, the other prominent gas, besides helium and hydrogen, that exists in these diffused nebulæ!" There is now nearing completion at Harvard a catalogue of the spectra of 225,000 stars, a catalogue of the classification of the stars on the basis of their chemical composition.

"A more glorious universe remains. We are courageous then

as to our problems, and we are also without fear, for the astronomer's faith is well expressed by that famous epitaph of Dr. John Brashear, 'he loved the stars too dearly to be fearful of the night.' "

## PROCEEDINGS OF FRIDAY, SEPTEMBER 30

Beginning at 9.30 A. M., the entire morning was taken up with the reading and discussion of papers which, in part, formed the Symposium on Non-ferrous Metallurgy. The authors of the papers are as follows: H. M. St. John, T. F. Baily, N. K. B. Patch, Ernest A. Smith, H. A. De Fries, F. C. Thompson, R. J. Anderson, H. A. Winne, J. G. Thompson, M. L. Hartmann and W. A. Koehler, Haakon Styri. The papers are printed in full in these Transactions.

The outstanding social event of the afternoon turned out to be a rather wet one, and will be remembered for days to come by members of the party who started out with aspirations of climbing to the top of Mount MacIntyre. Several members, through great persistence and in spite of the unrelenting rainstorm, reached the summit.

In the evening Col. T. S. Woolsey, Jr., formerly in charge of all the technical forestry work for the United States Government, and during the war a member of the Inter-Allied Forestry Commission in Paris, entertained the members and their guests with a very interesting and instructive illustrated talk on "Forestry in Europe and America." Col. Woolsey emphasized the importance of caring for our virgin forests, and the necessity for stricter regulations in our country for reforestration. Natural regeneration, which has proved to be practicable in French forestry, will probably be used in this country where land is cheap but labor costs high. The interdependence of forests, water power and electrochemistry was repeatedly emphasized. "The great problem before us is timber supply..... It is a question of a century to grow good timber..... If you do not practice forestry it sometimes happens that the penalty is very great..... It is expensive and difficult to get back the forest growth after it once disappears."

The protection of forests from fire, the elimination of destructive insects, and the prevention of destruction of seedlings by

sheep and cattle were a few of the topics commented upon at length. The colored slides were exceptionally realistic.

### PROCEEDINGS OF SATURDAY, OCTOBER 1

Dr. Wm. Blum, of Washington, briefly informed the members that the Board of Directors had authorized the formation of an Electrodeposition Division, of which he was appointed chairman. The technical program for the morning included a Symposium on Electrodeposition. Papers were presented by F. A. Lidbury and F. A. Stamps, H. M. Goodwin and L. A. Wilson, W. E. Hughes, T. R. Briggs, W. R. Ingalls, C. J. Wernlund, Wm. Blum and H. E. Haring, Wm. Blum. These papers, with discussion presented, are printed in full in this volume.

In this, the concluding session, Dr. Carl Hering presented a Resolution of Thanks, expressing the high appreciation of the Society for the very kind hospitality accorded to its members and guests by the Lake Placid Club, and to the members of the arrangements committee, W. M. Corse, Chairman, whose efforts made the meeting most enjoyable to everyone.

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## PROFESSOR JOSEPH WILLIAM RICHARDS

Less than a fortnight after the close of the Lake Placid meeting, the sad news of the sudden passing away of Professor Joseph W. Richards reached the members of the Society.

Prof. Richards came of a long line of chemists and engineers, his grandfather, William Richards, having worked with Stevenson in England on the "Lion," one of the earliest steam locomotives, and also built the first one-span iron bridge across the River Wye. His father, Joseph Richards, was a metallurgical chemist and was awarded the John Scott medal of the Franklin Institute, Philadelphia, for the first successful solder for aluminium.

Dr. Richards was born in Oldbury, England, in 1864, and came to the United States at the early age of seven years. He was graduated from the Central High School of Philadelphia, Pa., in 1882, with the degree of Bachelor of Arts (A. B.) and entered Lehigh University in September of that year. In 1886 he grad-

uated from Lehigh University with the degree of Analytical Chemist (A.C.). He pursued graduate work at Lehigh University and was awarded the degree of Master of Science (M. S.) in 1891, and two years later Doctor of Philosophy (Ph. D.), the first bestowed on any of its graduates by his alma mater. He received the degree of Master of Arts (M. A.) from the Philadelphia Central High School in 1887. In September of that year Dr. Richards was apppointed assistant instructor in metallurgy and blowpiping at Lehigh University, and served continuously at the university from that time until his death in the following positions: Instructor in metallurgy, mineralogy and blowpiping, 1890-1897; assistant professor, 1897-1903; professor of metallurgy, 1903-1921.

As a man he was quiet, gentle, and the soul of honor. He was a splendid teacher and noted for his punctuality, many of the students actually telling the time of day by his comings and goings. He loved to teach, and would spend any amount of time on those who really wished to learn. He was a Unitarian, and as there was no church of this denomination in Bethlehem, he united with the First Unitarian Church of Philadelphia. His home was the center for much religious discussion among a circle of educated and thoughtful men and women. During the last year of his life he became interested in psychic religion, or spiritualism, and one of the last books he read with interest was Prof. Geley's "From the Unconscious to the Conscious."

He traveled a great deal during his life, and was an enthusiastic member of the National Geographic Society. A local geographic society met monthly at his own home, where he loved to have them, and often gave lantern talks himself. He was a connoisseur of pictures, and during the last ten years had collected a number of excellent canvases, notably two by the Scandinavian artists, Neumann and Hans Dals.

His greatest joy, outside of his work, was the Bach Choir, of Bethlehem, of which he was a charter member from its inception in 1905. He never missed one of the concerts of the annual Bach festivals in May, and knew how to appreciate and interpret the products of Bach's great genius. In early boyhood he had been taught by pious parents the hymns of the Methodist Episcopal Church, and he knew nearly every tune by its own particular name, an unusual feat in these days.

During the war Prof. Richards was a member of the Naval Consulting Board, of which Mr. Edison was chairman. He became a "dollar-a-year" man, closed his home, and with his wife and one daughter went to live in Washington, D. C., where for nearly two years he worked cheerfully and with patriotic ardor at his desk, eight hours a day, taking no vacation for two summers. It was his contribution to the country which had given him the opportunity to achieve success in his own line of work.

As a metallurgical engineer of international reputation his services were widely sought in chemical and metallurgical cases. He was a member of the United States Assay Commission, 1897; representative of the Franklin Institute to the International Geological Congress held in Russia in 1897; member of the jury of awards, department of chemistry, of the National Export Exhibition, Philadelphia, in 1899; member of the jury of awards and chairman of the metallurgical sub-jury, Panama-Pacific International Exposition 1915. He was a charter member of our Society, its first president, 1902 and 1903, and its secretary since 1907, in which capacity he served most conscientiously and indefatigably up to the time of his death. He was a member of the Franklin Institute, Philadelphia, president of the chemical section, 1897, 1899, and professor of electrochemistry of the Institute, 1907-1910. He was a member of the Faraday Society, Deutche Bunsen Gesellschaft, American Chemical Society, American Institute of Mining and Metallurgical Engineers, former vice-president of the Institute and chairman of the iron and steel committee since 1914; member of the Iron and Steel Institute of Great Britain, of the American Iron and Steel Institute, of Societe de la Chimie (France), of the American Institute of Chemical Engineers; honorary member of the American Electroplaters' Society. He was a member of the Board of the Engineering Foundation and a member of the National Research Council. He was the representative of the American Institute of Mining and Metallurgical Engineers on the joint conference committee of the Federated Engineering Societies.

Dr. Richards was a member of the Chemists' Club (New York), the Engineers' Club (Philadelphia), and the Niagara Club

(Niagara Falls). He was the author of a treatise on Aluminium in 1887, the only treatise on that metal in English; of the revised third edition in 1895; of Metallurgical Calculations, Part 1, and General Metallurgy in 1906; of Part 2, Iron and Steel, 1907; of Part 3, Non-ferrous Metals, 1908; also of Articles on Metallurgy in Chandler's Encyclopædia, and of many contributions to the Society's Transactions and other scientific journals. He was the translator of books from German and Italian entitled "Electrolysis of Water," "Electrometallurgy of Chromium," "Arrangement of Electrolytic Laboratories," "Electrolytic Production of Metallic Objects," "Cementation of Iron and Steel."

Dr. Richards died suddenly, October 12, 1921, of an organic affection of the heart, beloved by his family and a world-wide circle of friends, and greatly respected by his Alma Mater, where he had taught for thirty-five years, and by all the numerous scientific societies of which he was a happy and enthusiastic member.

The Society held an extraordinary meeting in New York on November 16, 1921, in honor of the memory of Professor Richards. His life and achievements were fittingly conveyed in addresses by Professor W. S. Landis, for many years an associate of Professor Richards, Dr. Carl Hering, President Acheson Smith, Dr. H. C. Parmelee, of the McGraw-Hill Publishing Co., with whom Dr. Richards had been connected, and Dr. Florence Richards.

## DISCUSSION ON RECENT ELECTROMETALLURGICAL DEVELOPMENTS IN SCANDINAVIA

By Joseph W. Richards

I, personally, am interested in the Söderberg continuous self-baking electrode, and while in Norway this summer I saw a ferro-silicon furnace at Fiskaa, near Christiansand, which was operating with one round and one rectangular electrode. From observation, the operation of the two electrodes appeared exactly alike, so that the practicability of using the continuous self-baking electrode in the rectangular furnace was demonstrated on a scale of about 1000 Kw. on each electrode.

At the Stavanger Steel Co., on the western coast of Norway, the Söderberg electrode is being used on a tilting Heroult steel furnace, and its operation has proved very satisfactory. They found that it was difficult to get workmen to get on top of the furnace and make a good connection, owing to the intense heat of the furnace. Therefore, when an electrode got short it was taken out of the furnace and a longer one put in its place. The electrode stumps were taken over to a corner of the building where they were half buried in sand, and connections were carefully made there. They found it profitable to make connections in this manner, as they could make them so much better than over the furnace, where they had to work rapidly on account of the heat of the furnace. They adopted the same scheme for the Söderberg continuous self-baking electrode. When the electrode became short it was taken out of the holder and a longer one put in its place. A new shell section was welded on to that of the electrode stump and filled and stamped ready for use. In other words, the electrode was simply replaced in the furnace as it became short, and the lengthening was done, not at the furnace, but in the corner of the building. In that way there was no additional complication whatever to the working of the furnace. The consumption was the same and there was no more apparatus needed than usual. The sections put in were seven feet long, so that there was a considerable addition to the length. Those I had previously seen put on were between three and four feet long. On one occasion they did not have a partly baked electrode ready to put in, so they used an entirely green electrode,

that is, a casing filled with the green material, unbaked carbon paste. This electrode, when put in the furnace, worked satisfactorily and served as an experiment.

CARL HERING: How did they weld on to the stump?

J. W. RICHARDS: They had a long casing, say twelve or fourteen feet long to begin with, and in the starting of the furnace they usually baked the lower end of the electrodes before putting them in. In this case, however, the electrode was entirely green down to the point where they put it in the furnace, and it worked.

A MEMBER: Was that a furnace with molten steel in it, or were they starting a heat from a cold charge?

J. W. RICHARDS: In this furnace they had molten steel. I saw several of the Söderberg electrodes in use in a six-ton furnace, and apparently they are working all right in this tilting furnace, at a length of fully one meter, from the roof down to the steel.

At another one of their experimental stations I saw a continuous electrode which was being used on an aluminum pot. This electrode was made large in diameter, as they prefer the large electrodes in Scandinavia. In fact they use electrodes up to 18 inches square, whereas in this country the regular size for aluminum cells ranges from three to six inches in diameter. They will have to work out a good many details before they can apply an electrode which will work continuously on the aluminum bath. In their experiment they used an aluminum casing; the pot was about 20 inches square and the electrode 18 inches square so as to nearly fit the mouth of the pot. There is a holder around the lower part of the electrode which chills the aluminum casing and keeps it cool. Below the holder the electrode is baked sufficiently hard. One very interesting point which could not have been predicted is that the electrode burns up very nearly level; there is hardly any point to it. When I saw it, it was very slightly convex, but it usually burns almost perfectly flat at the bottom.

A MEMBER: I understand that their method involves the welding of the aluminum casing.

J. W. RICHARDS: They had been riveting it, but it is still to be worked out whether it should be soldered, welded or crimped

on. In fact, they were sending the current in not by the holder, but by the aluminum casing. This was entirely experimental and is about half way advanced towards successful practice.

Up in northern Sweden (I went all the way up to Lapland) there was a very interesting power plant at Porjus. There are rapids on a large stream running from the mountains east, and at Porjus they have an admirable power plant. I am not enough of an electrical engineer to know all the details of different power plants, but it struck me as being admirably constructed. The fall there is 50 meters, about 160 feet, with rapids running down for about two miles; they have a tunnel, like the Niagara Falls tunnel to the rapids. Their tunnel is about 2 miles long. The entire power plant is cut out of the rock at the upper level, and the housing of all machinery is 150 feet under ground, corresponding to our upper Niagara plant, except that they put all the machinery down at the level of the tail race. They said that one great advantage was that there was no building to construct, and in that severe climate the whole machinery being under ground they had no surface troubles. Below Porjus there is still a larger falls called the Harspraang, where there is a one hundred meter fall in a distance of five miles; they were constructing a tunnel five miles long for a tail race, and this whole plant is to be sunk 330 feet under ground.

F. A. LIDBURY: Are they using horizontal or vertical turbines?

J. W. RICHARDS: They are using horizontal turbines. The minimum flow at the upper plant amounts to eighty thousand kilowatts, and that is to be just about doubled for the lower plant when completed. They are regulating the flow of the river at a point six miles above Porjus in order to increase the flow about 50 percent, so that their minimum would correspond to 120,000 Kw. at the first plant and 240,000 in the new plant. The interesting point was that it was 60 miles from Porjus up to where they are building the regulating dam. The engineer, Mr. Sundblad, is the man who built the power plant at Trollhätten. He had to make frequent visits up to the regulating dam, and ordinarily it took him two days to get up there, and still longer in the winter. Accordingly he got a flying machine and went up in forty-five minutes. Everything about the plant was most admirably planned and constructed. It looked like one of our

model Niagara Falls plants; there was no necessary expense saved, but there were no unnecessary frills that I could see on any of the work. Five years ago there was not even a road into this place, it was nothing but a path, and tourists would spend a couple of days getting there to see these water falls; now there is a road and a railway there. I met one of our men, a Mr. Victor Thrane, who sent his regards to his friends over here. He took me into the sodium plant he is operating, but I am not at liberty to tell all that I saw there. He had units of 4000 amperes capacity, the largest sodium pots I ever saw. It was a very nice little plant. His difficulties are with the freight rates from this out-of-the-way place. Before the war he thought he was favorably situated, but when the war came on the freight rates went up to two or three times what they were before. It made it pretty difficult to compete with other plants which are at sea level and have cheap freight rates.

F. A. LIDBURY: How far are they away from tidewater?

J. W. RICHARDS: From Porjus it is about 150 miles to Narvik and 300 miles to the head of the Baltic, but the head of the Baltic is frozen over six months in the year. They had two electric pig iron furnaces that they had put up there, and they figured out that they had the iron close at hand and had cheap power, but they did not reckon with the freight rates going up as high as they have gone, so the plant was shut down and will have to be moved to an ice-free harbor.

C. G. SCHLUEDERBERG: How far are they transmitting the power at this time?

J. W. RICHARDS: When they get the whole thing developed, it will be about 400,000 Kw., and their intention is to distribute it over the whole northern part of Sweden down to Stockholm, six hundred miles away. They said they were going to raise the voltage to 300,000 volts and distribute the power to all the towns and cities down to Stockholm.

ACHESON SMITH: Did they quote any prices on power there?

J. W. RICHARDS: The prices on power quoted were in the neighborhood of $5.00 per kilowatt year.

ACHESON SMITH: They could not produce it for that?

J. W. RICHARDS: I will say this, there are a number of places

in Norway and Sweden where they have power at that price; that is on the old contracts.

CARL HERING: Is this an installation by the government or by private parties?

J. W. RICHARDS: I have an idea it is by private parties; they are electrifying the railway all the way from the head of the Baltic to Narvik on the Norwegian side. On these admirable trains they run 30 ore cars of 38 tons each, or 1000 tons of ore altogether to a train. The cars are well constructed, excepting that the couplings are little fliver buffers such as they have on their passenger trains, and the brakeman has to creep under and get in between to couple the cars; the buffers have springs as on their passenger cars. They found it impossible to put in American self-coupling service, and in order to run the new cars on the Swedish railways they had to put the same couplings on the ordinary freight cars as on the passenger cars.

ACHESON SMITH: The question of power in Scandinavian countries is quite a problem. I made some inquiries in Norway and was absolutely unable to find any power as low as $11.00 per kilowatt year. That was about ten years ago, when I was in the position of a prospective customer. I doubt if power could be had today in plants like that for less than $15 or $20.

J. W. RICHARDS: Those who had contracted, say at 50 crowns a kilowatt year, that used to be $13.00; but at the present time it is only about half that much on account of the exchange. I should have made that explanation.

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*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# EXPERIENCES WITH THE ALKALINE AND ALKALINE EARTH METALS IN CONNECTION WITH NON-FERROUS ALLOYS.[1]

By Charles Vickers.[2]


## Abstract.

Sodium, of the alkaline metals, serves as a suitable deoxidizing agent in producing copper castings of superior torsional strength. Calcium, of the alkaline earth metals, when in combination with an acid element, as silicon, produces castings of good electrical conductivity. Barium and strontium according to the author's experiences require a vast amount of research work in this connection. [A. D. S.]


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## ALKALINE METALS.

A survey of the alkaline group of metals reveals only one having possibilities in connection with the casting of copper and its alloys. This one is sodium; the other members of the group are too rare and expensive for such commercial use. However, it is doubtful if potassium, rubidium or caesium could be used on account of their low melting points even if plentiful and cheap.

The low melting point of sodium is a big drawback to its use as a degasifier of pure copper, as the temperature of molten copper is sufficiently high to volatilize the sodium with explosive violence. Repeated attempts to "deoxidize" copper with metallic sodium made by the writer have failed. The sodium would ignite and burn away on the surface of the copper, with the result the latter when poured into molds produced porous castings, quite as though it had never been treated. It may be asked, why not enclose the sodium in a copper capsule, or use a phosphorizer, and

[1] Manuscript received August 15, 1921.

[2] Consulting Foundry Engineer, Buffalo, N.Y.

so plunge it underneath the surface of the copper? The answer is that it would not be prudent to attempt this, under ordinary foundry conditions. The actions of the sodium at the moment of contact with the copper suggests that an explosion would result if it were plunged underneath the surface. The experiment is worth making, but it should be carried out under conditions that would minimize the effects of the explosion should one occur.

The sodium acts similar to a damp poker when it contacts with the molten copper, and this so far has discouraged the thought of plunging it beneath the surface.

When first alloyed with other metals though, sodium can be added to molten copper or bronze; thus ferro sodium is used as an addition to aluminum bronze as a degasifier, but is liable to produce red-colored specks on the surfaces of the polished casting, and, while these specks may do no harm, they are considered undesirable. For adding sodium to bronze an alloy of sodium and tin is very suitable. This alloy is easily made; the tin is heated to a little above its melting point, and the sodium is added in small pieces with constant stirring. An alloy of 95 percent tin and 5 percent sodium is the most convenient, and it is used in bronze exactly the same as the 5 percent alloy of phosphorus and tin. At one time the writer made considerable quantities of an alloy of copper, 90 percent; tin, 5 percent; sodium tin, 5 percent. This alloy was used where torsional strength was desired. For this purpose it appeared superior to the regular phosphor bronze alloy of copper, 90 percent; tin, 5 percent; phosphor tin, 5 percent, previously used. The method of testing was a crude one—it was simply a foundry test. Experimental heats of the two alloys were carefully made with a view of having the melting conditions as nearly the same as possible. A pattern for a flat bar was made and molded in sand. This pattern was 14 inches long, 1⅛ inches broad by ⅜ inch in thickness, and a casting was made from each alloy. The tests were conducted by clamping one end of the bar in a vice, with the bar vertical; a wrench with a 13-inch purchase was adjusted on the upper end horizontally, and two men twisted the bars to destruction.

The phosphor bronze bar invariably broke at one, to one and a half turns; after 2½ complete twists the sodium bronze bars

became so stiff they resisted the strength of the two men at that leverage. A softer alloy was then made of both alloys, the phosphor bronze contained copper, 95 percent; phosphor tin, 4 percent; tin, 1 percent. The sodium bronze bar contained copper, 95 percent; sodium tin, 4 percent; tin, 1 percent. The phosphor bronze bars twisted off at one complete turn. The sodium bronze bars broke at three complete turns. Accordingly, the sodium bronze was decided on as the material for the castings. Sodium tin, however, is not as convenient for foundry use as phosphor tin, as the sodium oxidizes out of the tin, attracts moisture from the atmosphere, changes to the hydroxide, and covers the metal with a slimy wetness; in fact, one percent sodium tin can be used as a metallic soap. Should the wet tin be added to molten metal an explosion would result. The alloy should be stored in air-tight receptacles, and before use it should be warmed; it will then hiss and spit a little when added to molten copper, but there is no danger from flying metal.

## ALKALINE EARTH METALS.

The alkaline earth metals, calcium, strontium and barium, present no difficulties when used to alloy with copper. Calcium alloys in all proportions with copper, but the alloy of 50 percent copper, 50 percent calcium, is not stable when exposed to the atmosphere. It is a silvery white alloy that rapidly tarnishes and becomes black, then falls to a black powder; it should be kept in air-tight receptacles, or, better still, used to make a 10 or a 15 percent calcium copper alloy that is hard, brittle and perfectly stable.

The 50:50 copper-calcium alloy is a powerful reducing agent and mixed with either sodium hydroxide or sodium chloride, the mixture can be ignited with a match, especially the former burning with a sudden, intense light. The presence of metallic sodium is shown when the reduced material is thrown onto water. The experience with calcium covers a period of some ten years; the early supplies of calcium were obtained from Germany and came in 25-kilogram lots in the familiar cabbage-stalk form in sealed tins. The specific gravity of the German calcium was 1.52, melting point, 1,400° F., according to my notes, and the analysis showed the presence from 0.2 to 0.5 percent silicon, and from 0.25

to 0.30 percent of aluminum. Later, some General Electric produced calcium was obtained; it was put up in brass tubes, and still later the 50:50 calcium copper was used.

The first experiments were made using an alloy of copper and calcium made by embedding five ounces of calcium in 95 ounces of granulated copper in a crucible. The mixture was then covered with a thick layer of charcoal and was melted as quickly as possible in a wind furnace. The resulting alloy was brittle, hard and brassy and flowed somewhat sluggishly. Analysis showed 3.59 percent calcium. When made this way the loss was found to be higher than when the copper was first melted under charcoal, and then the calcium added by simply throwing it onto the surface of the copper, and pushing it under and stirring. Hundreds of pounds of 10 and 15 percent calcium copper were made satisfactorily in this rough and ready fashion.

This calcium-copper was used to make copper castings, using at first 1 percent calcium copper. The first test was very satisfactory, the castings being sound and clean, but a second test failed to duplicate this result, the castings being porous, although made in the same manner, and finally as a result of a large number of tests it was found that calcium alone could not be depended upon to produce sound copper castings on a commercial scale. When the term castings is used in this paper, it must be understood that sand molded castings are alluded to in all cases. When non-ferrous metals are cast into molds of metal or carbon the result is entirely different to when cast in sand, and no reliable opinions can be formed regarding their behavior in the foundry. A metal that cannot be cast in sand molds has little value as an engineering material, as it is limited to rolled, drawn and extruded shapes. Thus the difficulty experienced in making castings of aluminum bronze seriously limits the use of this otherwise valuable alloy.

In the calcium tests 40 grams of metallic calcium was added to 100 pounds of molten copper; the calcium was added to the copper after the latter was removed from the furnace, and it was stirred into the molten metal. The result was a failure; the castings being porous. These experiments were repeated a number of times; the experienced brassfounder can very quickly decide whether a deoxidizer is a success or a failure in connection with

the casting of copper. Calcium is considered to have been proved a failure with copper; once in a while a sound casting was obtained, but the great majority of castings came out apparently sound and clean, but under the skin the structure was cellular, the holes being uniform in size, small and usually round. In the case of aluminum bronze a few hundredths of a percent produces a dull, brownish-colored exterior on the castings, and inside, when cut, there will be found tortuous holes, like worm holes in rotted timber. The inside of these holes is usually colored a rather dark brown. When lime is used as a flux on aluminum bronze, enough calcium will be reduced to produce these worm holes, and skin discoloration. Hundreds of tests were made with calcium in aluminum bronze, which resulted in the discovery that calcium must be used in homeopathic doses, combined with manganese and magnesium in proper proportion, and when so combined it will prevent the difficulty of worm holes, and pear-shaped holes in aluminum bronze castings.

As a result of a large amount of research work, it was found that calcium should be combined with silicon for use as a deoxidizer of copper for sand castings. Thus an alloy of silicon, calcium and copper was produced. The percentage of silicon varied from 7 to 10 percent, that of the calcium from 3 to 5 percent. This is the alloy that was used to densify the copper castings described in a paper before this Society by Geo. F. Comstock[3] some four years ago. This alloy, however, proved very much of a failure when placed on the market, as the results obtained in casting copper by its use were spotty. It is still being made, but only 46 pounds have been sold in the United States during the first six months of 1921. The failure of this alloy led to further experimenting, which resulted in the addition of a third element to the calcium and silicon. This made an immediate improvement, but it required months of cutting and trying before the proportions were adjusted to give the best results. At present this triple alloy is very successful in producing copper castings of high electrical conductivity; by its use a conductivity of 85 per cent can be consistently expected measured on the casting. I regret that I am not at liberty to make known the composition of

[3] Trans. Amer. Electrochem. Soc., 1917, **32**, 221.

this alloy. The alkaline earth metals, however, play a very important part in its composition and have greatly helped to solve the problem of producing high conductivity cast copper. I say "helped to solve" advisedly, for in spite of the alkaline earth metals and the help of boron, the problem is still with us; if the copper and the degasifier are not handled skillfully the results will be disappointing. In addition to its value in making copper castings, this triple deoxidizer has proved excellent in the case of monel metal, and other high nickel alloys, where the problem is very similar to that of copper.

### CALCIUM IN BRONZE.

A large number of experiments were conducted with calcium in copper alloys; the calcium was used alone, when combined with manganese, titanium, and phosphorus, and it was added in the shape of calcium copper, calcium tin, calcium lead, and calcium zinc. We have space for only the tests with calcium copper. The alloy in which the calcium was tried consisted of copper, 88 percent, tin, 10 percent, and zinc, 2 percent. The calcium copper used was made to contain 10 percent calcium, analysis showed 6.36 percent calcium. In the first test the bronze was re-melted and was deoxidized when liquid and ready to pour by the addition of 0.5 percent of calcium copper containing 6.36 percent calcium.

An average of three test bars pulled gave the following results:

| | Average of 3 Bars |
|---|---|
| Tensile strength lb. per sq. in | 39,130 |
| Elastic limit, lb. per sq. in | 20,600 |
| Elongation, percent in 2 inches | 13.0 |
| Reduction of area, percent | 14.7 |

In the second test the bronze was re-melted and one percent of 6.36 percent calcium copper was added, with the following results:

| | Average of 3 Bars |
|---|---|
| Tensile strength, lb. per sq. in | 38,200 |
| Elastic limit, lb. per sq. in | 21,800 |
| Elongation, percent in 2 inches | 11.3 |
| Reduction of area, percent | 11.6 |

The fractures of the broken bars showed traces of "segregation." They were not homogeneous.

The above tests were made on sand cast bars, made cast-to-size with risers and gates on the ends of the grips. A thin skin was machined off the bars to make them true. The untreated alloy cast under the same conditions gave the following results:

| | Average of 3 Bars |
|---|---|
| Tensile strength, lb. per sq. in. | 38,770 |
| Elastic limit, lb. per sq. in. | 21,600 |
| Elongation, percent in 2 inches | 11.2 |
| Reduction of area, percent | 15.0 |

The tests with calcium have been carried on over a period of years, and the result has been that with the exception of the alloy used for copper and monel metal, and which on account of its silicon content is of no value for bronze, there is no calcium alloy now being used as a deoxidizer in brass and bronze.

The experiments with strontium and barium were at first conducted with alloys of barium and tin, and strontium and tin. These were produced by the decomposition of barium or strontium chloride by sodium dissolved in tin. A 5 percent alloy of sodium tin was first made, and to this the chloride was added little by little. The resulting alloys would contain as a maximum 2 percent of barium or strontium. Later the barium tin was made by electrolysis at Columbia College and alloys of barium tin containing 5 percent, and 10 percent barium were made, also alloys of barium and aluminum. Both the 10 and 5 percent alloys of barium and tin are perfectly stable; the 10 percent alloy forms a coating or scale which is detached from the core of metal. This scale when filed shows metallic, however. As far as the tests with barium have gone it has been proved that a vast amount of experimental work is necessary before it can be honestly offered to the trade; one thing has been determined, barium has no favorable effect on the drossing of aluminum bronze, neither will it favorably affect the porosity of aluminum castings. Its usefulness appears to be limited entirely to brass and bronze, but just how useful it may be can only be determined by means of long and expensive research.

## SUMMARY.

Of the alkaline group of metals, sodium is the only one that has been tested. It appears to have a negative value for copper,

but has some points of superiority over phosphorus in deoxidizing bronze, as it appears to produce an alloy of superior torsional strength. Of the alkaline earth metals, calcium appears valueless in connection with producing solid copper castings, and to have a negative value in bronze. As a deoxidizing agent in copper, calcium is at its best when combined with an acid element, such as silicon, and this combination is improved by a third element. This latter combination is being used with success for the production of copper castings possessing high electrical conductivity. Barium and strontium appear slightly more promising than calcium, but a large amount of foundry research work is necessary before their actual value is known.

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## DISCUSSION.

COLIN G. FINK[1]: Mr. Vickers refers to the difficulties he has had in using calcium and barium, and mentions time and again that the castings he obtained were full of blow holes and full of calcium oxide, etc. On the basis of the few experiments we have made, it is important to take into account the products that calcium will form, and the relative melting points of these products. For example, if we use calcium as a deoxidizing agent, we will form calcium oxide as the first product, and the melting point of calcium oxide is so high that it will not flow; the oxide will stick right in the metal; so the idea is to add some other element to the calcium in order to form low-fusing products.

WM. BLUM[2]: Mr. Rawdon showed that when sodium is introduced into copper, as happens when copper is "pickled" in a fused sodium-chloride bath, the sodium causes brittleness.

J. W. RICHARDS[3]: It is not so much a question of the material floating, but a question of its segregating, so as to free the metal from the oxides. If the resulting oxide has a higher melting point than the prevailing temperature, then the finely divided

[1] Consulting Electrometallurgist, New York City.
[2] Chemist, Bureau of Standards, Washington, D. C.
[3] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

particles will not segregate, and that prevents them from coming up; they remain in suspension. The melting point of bronze is lower than copper, and the melting point of copper is not very high, 1084° C. Your calcium oxide has a melting point of 2570° C. Your calcium oxide mixed with silicon-oxide has a melting point of 2750° C.; calcium mixed with silicon may have a melting point of 1350° C. Still, that is high for casting copper; therefore, it is necessary to have another oxide in there, which, with the calcium-oxide and silica, will form a still more fusible material, melting and segregating and therefore eliminating itself at the temperature prevailing, which may be 1200° for copper and 1000° for bronze. These are the actual figures.

C. G. SCHLUEDERBERG[4]: I would like to ask the author whether the scheme works? Does this scheme claim to be better than that advocated a few years ago by Weintraub (boron sub-oxide)?

J. A. SEEDE[5]: I wish to ask the author if he can give us the temperature at which this new alloy is used, or if it is used at a lower temperature than boron sub-oxide.

CHARLES VICKERS (*Communicated*): With reference to Dr. Fink's remarks, no mention of calcium oxide in the castings is made in the paper. The castings deoxidized with calcium alone were filled with gas holes, but no blow holes. There were neither blow holes nor oxide in any of the castings where calcium was used simply as a deoxidizer. The castings were porous, that is completely permeated in every part by exceedingly fine gas holes. In some cases these holes were so fine they resembled little glittering crystals to the unaided eye, but a magnifying glass showed their true character.

Castings alloyed with calcium and cast in sand molds would show a thin film of calcium oxide externally. The drawback to calcium, because of the infusibility of its oxide, is not peculiar to calcium alone; the same thing exists with silicon, magnesium, aluminum and other elements when added to molten copper. These oxides largely remain in the copper and are a source of loss to the founder. Thus in making aluminum bronze, the first

[4] Asst. to Manager, Supply Dept., Westinghouse Electric & Mfg. Co., E. Pittsburgh, Pa.

[5] Electrical Engineer, General Electric Co., Schenectady, N. Y.

addition of aluminum acts as a deoxidizer, alumina is formed, which in slowly cooled castings will be found on turning them off, under the skin in little pools as a soft white substance that smears when the tool passes over it. When the casting is chilled the oxide is not noticeable, as it is then not collected together, but is dispersed throughout the mass of metal. If some second element could be found to add to any of these elements to form low fusing products upon oxidation, it would materially help to secure clean and sound castings.

When metallic sodium in alloy is added to copper the result is not brittleness. Bronze castings weighing several hundred pounds have been repeatedly made in which sodium was used as a deoxidizer and desulphurizer. These castings were not brittle. May not the action of a sodium chloride bath be similar to that of salts of mercury? Samrit bronze contains over 2 percent mercury, and samples of this ancient alloy supposed to be thousands of years old are still in existence.

In answer to Mr. Schluederberg's question I would say that the alloy finally arrived at appears to work successfully with copper. Copper castings of several thousand pounds weight have been made by its use. The alloy appears to produce results comparable in every way with the boron method of Weintraub. The alloy merely offers to the foundryman another pathway to the goal of high conductivity copper castings. If he fails with the one method he can try the other.

It has been the writer's experience in deoxidizing molten metals that better results will be obtained by the average founder with a doxidizing agent alloyed or incorporated with copper so that it can be added as a piece of metal, than with one that is added as a powder, and especially when the powder is an oxide and not metallic.

The above is not intended as a criticism of the products of boron used for the same purpose as this alloy. Those who have mastered the difficulties incident to the use of a non-metallic substance get excellent results. The writer during his experience as a foundryman has made hundreds of tons of copper castings, both mechanical and electrical, and realizes how thankful he would have been in the days before silicon, magnesium, alumi-

num, calcium, etc., were known, if some method of making clean, sound copper castings had been known, even though electrical castings were not asked for in those days.

In trying to devise an alloy for the purpose of making pure, sound, copper castings, it should be kept in mind that most of those who will use it are not technical men. While they are skilled in their particular work, the more foolproof the purifying alloys can be made the better they will work. Greatly superior results in the way of sound, clean, high conductivity, copper castings can be obtained by combinations of other elements than silicon and calcium, but it was always found that such combinations, while leaving nothing to be desired when used under the supervision of a metallurgist, would fail entirely when used by an ordinary furnaceman. The latter would mix his successes with failures, because of neglect through ignorance, and not intentionally.

With reference to Mr. Seede's discussion, no pyrometer readings have been made of the temperature at which the alloy is used, but the copper need not be superheated, as the melting point of the alloy is sufficiently below that of copper and dissolves easily. The copper should be melted under charcoal to a temperature at which it will appear thoroughly liquid when the covering is pushed aside to expose the surface. Such copper will appear bluish under the charcoal. If it is filmed over like bronze, and bubbles or boils, as it is termed, it will never make sound copper castings with any deoxidizer. It must be limpid and quiet under the charcoal, and then good results will follow. Ordinarily the foundryman will not superheat his copper, and as this alloy can be used at the temperature to which he is accustomed, many foundrymen prefer to use it.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# THE ELECTROLYTICALLY-PRODUCED CALCIUM-BARIUM-LEAD ALLOYS COMPRISING FRARY METAL.[1]

By Wm. A. Cowan, L. D. Simpkins and G. O. Hiers.[2]

## Abstract.

An account is given of the development of Frary metal and of its production by electrodeposition from a low melting point mixture of calcium and barium chlorides over a bath of molten lead as cathode. Metallurgy of binary and ternary alloys of calcium, barium and lead is described for portions of these series rich in lead, and photomicrographs are shown. The characteristics and properties of Frary metal are compared with those of other bearing metals, and the forms in which it is used are given. Excellent value as a bearing metal is shown in its having desirable hardness and strength, particularly at elevated temperatures, together with necessary plasticity.

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The complete thermal equilibrium diagram of calcium-lead alloys has been published,[3] but the barium-lead alloys and the ternary series of calcium-barium-lead have been studied and produced only through a range of composition covering the alloys rich in lead. The addition of only small amounts of calcium and barium makes a remarkable change in the properties of lead, particularly in its hardness.

During the early part of the world war when, on account of the large amount of shrapnel bullets being made from antimonial lead, there was a shortage of this material, and of antimony, a substitute was eagerly sought. It was following this that Drs. F. C. Frary and S. N. Temple procured patents[4] covering alloys

[1] Manuscript received, August 23, 1921.

[2] National Lead Company, Research Laboratories.

[3] "Tabellen," Landoldt, Bornstein & Roth. 1912 edition, p. 664.

[4] U. S. Patents, Nos. 1,158,671-5.

of lead with barium, calcium and other elements. The demand for hard lead for shrapnel bullets fell off, owing to the increased use of gas shells, before the calcium-barium-lead alloy was fully developed for this purpose. However, the alloy was found to have remarkable qualities as a bearing metal, showing the characteristic structure and necessary properties required for such service. During the war, while there was need for conservation of tin, it was developed for this use. The Bureau of Standards made a report of physical and service tests on a submitted sample of the alloy showing better results than with genuine babbitt, and stating that it possessed all the requisites of a good bearing metal.[5] The alloy has been manufactured on an extensive scale for this and other uses by the United Lead Company.

## METHOD OF PRODUCTION.

The method of production of this type of alloy can be classified under the subject of electrodeposition from fused salts, since the process consists in electrolyzing the fused chloride of barium and calcium over a bath of molten lead as cathode. A molten lead cathode has been used for the production of metallic sodium, in early experiments by various investigators, as a carrier for the sodium, the latter being afterwards distilled off. In the preparation of alloys of barium and calcium by this method the electrodeposited metals are taken up by the lead, and the resulting alloy obtained as the desired product. There has been previous mention made in the literature of similar methods of preparing either pure metals or alloys by electrolysis of fused salts.[6] Such elements as sodium, calcium, magnesium, zinc and aluminum have been prepared as pure metals in this way, the principle involved being essentially the same in all cases, but differing in difficulties encountered. These are owing to differences in melting points and dissociation phenomena of the salts, as well as to differences in the properties of the pure metals produced. The preparation of metallic calcium from fused calcium

[5] Bureau of Standards, "Report on Tests of Ulco Hard Metal" to National Lead Co., May 6, 1918.

[6] Transactions of the American Electrochemical Society, 1906, **9**, 123; 1910, **17**, 249; 1910, **18**, 117; 1906, **10**, 63; 1909, **16**, 185. Metallurgical and Chemical Engineering, 1910, **8**, 253. Zeit. Electrochem., 1902, **8**, 817, 697. Electro-Chemical Industry, 1905, **3**, 63; 1905, **4**, 152. Transactions of the Faraday Society, 1906, **2**, 56.

chloride has been accomplished only after overcoming numerous difficulties. It was prepared on a fairly large scale during the war, and has also been made experimentally both by the Westinghouse Manufacturing and Electric Company[7] and by the General Electric Company. However, owing to the difficulties in producing pure metallic calcium free from chlorides, carbides and other impurities, it is not economical to produce an alloy by first preparing the calcium separately and adding it to molten lead. There would also be trouble in commercial manufacture of an alloy by mixing the pure metals in this way owing to the difficulty of obtaining complete solution of the calcium in the lead without loss by oxidation of the calcium. In attempting to produce metallic barium electrolytically it has been found that the resulting barium gathers around the cathode in small droplets which fail to coalesce, and therefore it is not economical to attempt to obtain the barium in a pure metallic state. However, with the use of a bath of molten lead as a cathode, this difficulty is not encountered, since the barium alloys readily with the lead as it is produced.

## MANUFACTURE.

Calcium-barium-lead alloys suitable for bearing metals and other purposes, together with the process of manufacture, are described in United States Patents.[8] The process of manufacture, as carried out by the United Lead Company operating under these patents, consists in the use of a series of iron pots of about two tons capacity each. These are partially filled with pig lead of high quality. Each pot of the series is set in a brickwork containing a hearth which is fired with coal. After the pots have been filled with pig lead all the hearths are fired until the lead is melted. On top of the molten lead is placed a layer of the mixed salts of calcium and barium chlorides of high purity, in such proportions as to give a low melting point. This layer of chlorides is usually about three to four inches thick. Each pot is equipped with a graphite anode at the center which can be raised or lowered by a chainblock.

In starting, the anodes are inserted in the chlorides, and a direct

[7] "The Electrolytic Production of Calcium," P H. Brace, Trans. Am. Electrochem. Soc., 1920. **37**. 465.

[8] U. S. Patents, Nos. 1,360,339 (T. F. Wettstein); 1,360,348 (G. H. Worrall); 1,360,272 (E. A. de Campi).

current thrown on. There is sufficient resistance in the salts to produce enough heat to fuse the mixed chlorides. The temperatures in the pots are controlled by raising or lowering the anodes. Under the influence of the electrolytic action, the fused salts are decomposed and the resulting calcium and barium are absorbed by the molten lead. There is a tendency towards fogging and arcing, and considerable amounts of the calcium and barium form carbides which reduce the efficiency of the process, therefore requiring approximately three days of electrolysis to produce a lead alloy containing 2 percent of the alkaline earth metals. The fused chlorides and carbides tend to freeze at the surface, forming a hard crust, particularly around the periphery of the interior of the pots.

If this crust forms too near the anode it may need to be broken down in order to give proper conditions; otherwise, it is advantageous, acting as an insulator and thus preventing loss of current which might pass through the fused electrolyte from the anode directly to the iron pot instead of to the molten lead. The absorption of the calcium and barium by the lead appears to follow a logarithmic curve, that is, it requires much longer than three days to produce an equal increment of absorption of the alkaline earth metals. This is probably due to an equilibrium set up between the lead and the alkaline earth metal, on the one hand, and in the decomposition of and reactions in the fused electrolyte, on the other hand.

After the electrodeposition has been under way for some time, samples of the molten metal are removed, and the barium and calcium contents determined; additional samples being taken from time to time until the desired composition is obtained. When the proper amounts of calcium and barium have been absorbed by the lead, the current is shut off and the molten alloy run out from the bottom of each pot into a carrying ladle of equal capacity, which is conveyed by an overhead crane. By this means the metal from the whole series of pots is emptied into a large mixing kettle where it is thoroughly agitated and further alloying ingredients are added. The resulting alloy is then sampled and cast into ingots for shipment.

## FRARY METAL.

The alloy thus produced by the United Lead Company has been termed "Frary metal." As disclosed by the patents, it is essentially a ternary alloy of lead, barium and calcium, with the addition of small amounts of other elements. It contains up to 2 percent barium and up to 1 percent calcium, the remainder consisting almost entirely of lead. As much as 0.25 percent mercury, and smaller amounts of other elements may be added.

## METALLOGRAPHY.

In studying the metallography of the alloy it is most profitable to first consider the binary alloys, barium-lead and calcium-lead.

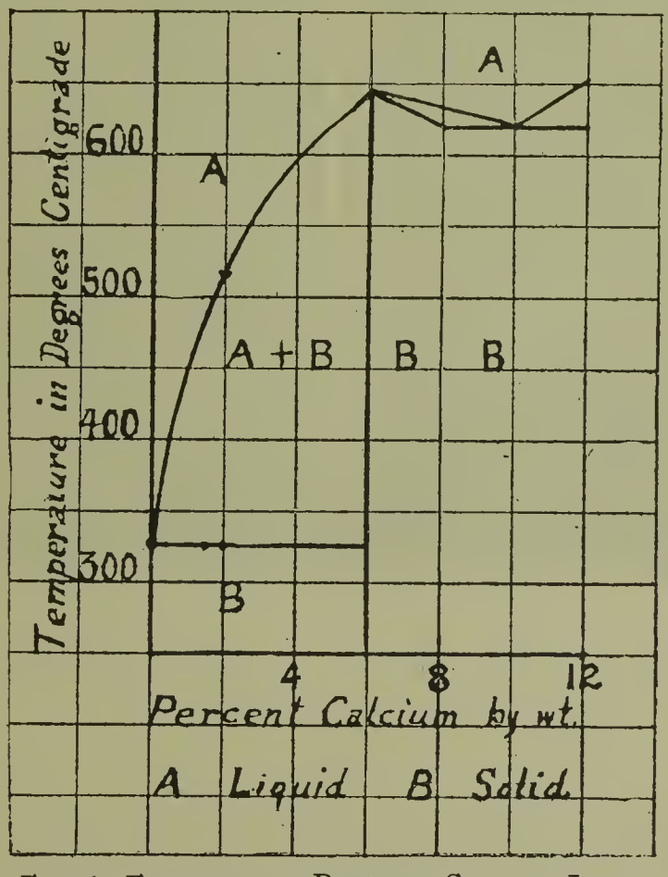



FIG. 1. EQUILIBRIUM DIAGRAM CALCIUM-LEAD.

The constitution of the latter series of alloys has been investigated by N. Baar[9] and L. Donski,[10] and a portion of the thermal equilibrium diagram, adjacent to the lead side, as published in Landoldt and Bornstein[11], is reproduced in Fig. 1.

Several points in the curve have been checked very closely by

[9] Z. anorg. Ch., 1911, **70**, 375.
[10] Z. anorg. Ch., 1908, **57**, 217.
[11] *Loc. cit.*

determinations made at this laboratory. It appears from the complete diagram that additions of calcium up to 6 percent where the compound $Pb_3Ca$ is formed, raise the melting point rapidly. Other compounds are formed beyond this and the melting point is increased to 1100°C. The photomicrographs, Figs. 2 and 3, are in accord with this equilibrium diagram. They show crystals of lead-calcium compound ($Pb_3Ca$) in a ground-mass of lead. The crystals appear to be rod or needle-shaped, and at higher magnification the rods are shown to be built up of cubical crystals, Fig. 12. Calcium-lead alloys for experimental purposes were made at this laboratory from pure lead and elec-

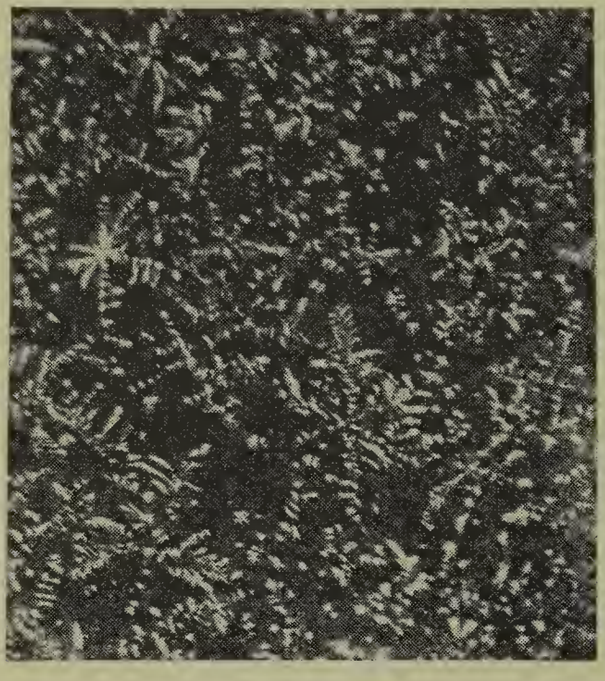


FIG. 2. CAST SPECIMEN.
Calcium 1.52 percent; lead, balance. Polished but not etched, showing lead-calcium compound ($Pb_3Ca$) in relief, in a ground-mass of lead. (x 50).

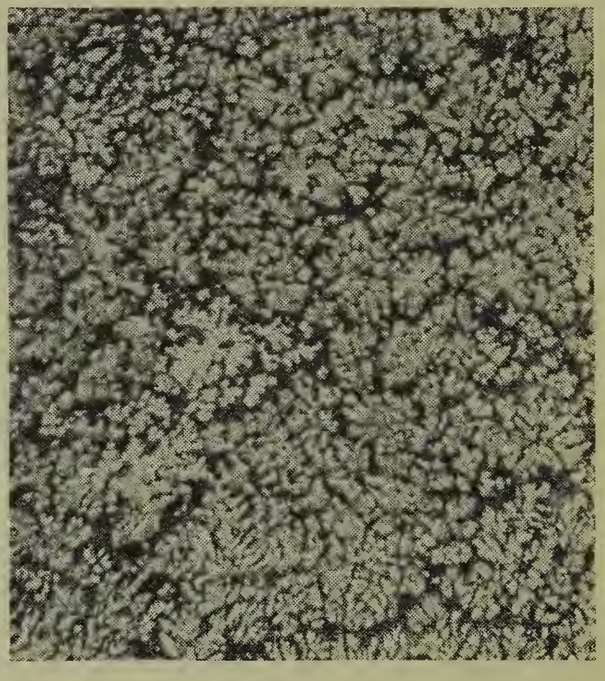


FIG. 3. CAST SPECIMEN.
Calcium, 3.20 percent; lead, balance. Similar to Fig. 2, but showing more $Pb_3Ca$. (x 50).

trolytic metallic calcium, the latter purchased from the General Electric Company. The lead is melted in a ladle and heated to about 500°C. A piece of calcium is then held under the molten lead, being scraped meanwhile to remove oxide, etc., and to allow the lead to come in contact with clean metallic calcium. When the calcium dissolves there is a decided exothermic reaction and more lead in bar form is quickly inserted in the molten metal to cool the alloy and prevent oxidation. In this way alloys containing up to 6 percent calcium were made up to be used as base metals in preparing other alloys for further in-

vestigations. Composition of the metallic calcium purchased, and an alloy made with its use are shown in Table I.

In studying the constitution of barium-lead alloys no published data could be found, but sufficient work has been carried out in this laboratory to give the thermal equilibrium diagram up to approximately 6 percent barium. An alloy was produced for us at the plant of the United Lead Company at Keokuk, Iowa, by the electrolytic process from fused barium chloride using molten lead as cathode. The results of analysis of this alloy are given in Table I. By diluting this with pure lead, alloys of varying compositions were produced for our investigations. Cooling curves

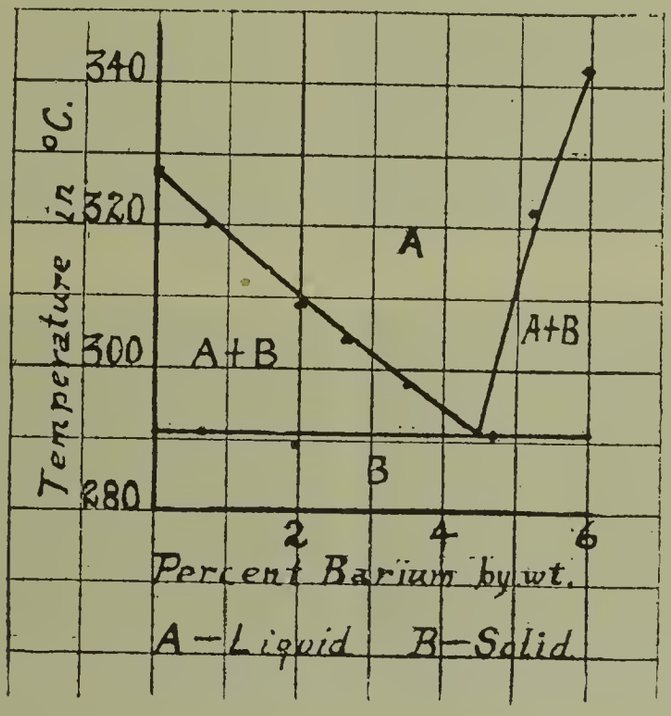



FIG. 4. EQUILIBRIUM DIAGRAM BARIUM-LEAD.

were determined both by the differential and the inverse rate methods. From the results obtained the equilibrium diagram shown in Fig. 4 was derived. After our work was completed an abstract appeared[12] describing an investigation of barium-lead alloys first published in Zeitschrift für Metallkunde, October 1, 1920.[13] Our work was in fact practically completed before that date, and is corroborated by the results reported in the article. Photomicrographs made at our laboratory (Figs. 5-11) are in

[12] Chemical Abstracts, Vol. 15, p. 662.

[13] "The Constitution Diagram of the Alloys of Lead and Barium," by J. Czochralski and E. Rassow.

## Table I.

*Composition of Metallic Calcium and Lead Alloys.*

| | Electrolytic Calcium—29193 Percent | Calcium-Lead Alloy—29868 Percent | Barium-Lead Alloy—29838 Percent |
|---|---|---|---|
| Lead | none | 96.43 | 93.17 |
| Barium | none | ..... | 6.05 |
| Calcium | 86.42 | 3.20 | none |
| Tin | ..... | ..... | trace |
| Antimony | ..... | ..... | 0.0017 |
| Copper | 0.16 | ..... | 0.0032 |
| Zinc | none | ..... | trace |
| Aluminum | 3.55 | ..... | none |
| Iron | | ..... | 0.0006 |
| Bismuth | ..... | ..... | 0.055 |
| Mercury | ..... | ..... | none |
| Magnesium | 0.29 | ..... | 0.0008 |
| Sodium | 0.55 | ..... | ..... |
| Carbon (by diff.) | 9.03 | ..... | ..... |

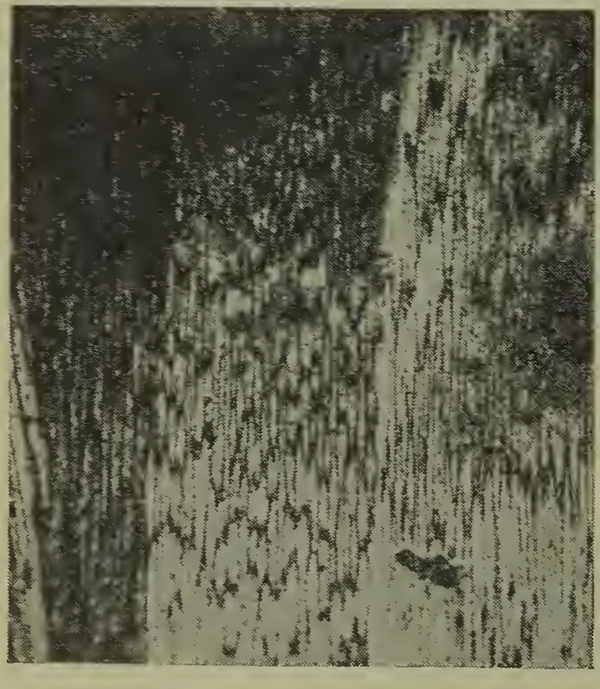


Fig. 5. Cast Specimen.
Barium, 0.50 percent; lead, balance. Etched with 2 percent $AgNO_3$ in $C_2H_5OH$. Showing presence of small amount of eutectic. (x 50).

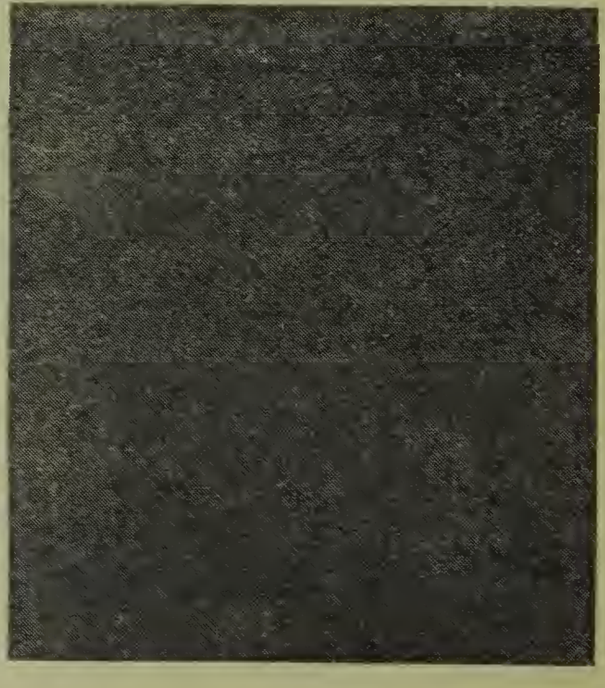


Fig. 6.
Barium, 1.39 percent, lead, balance. Polished but not etched, showing no hard constituents in relief. Lines shown are polishing scratches. (x 50).

accord with the thermal equilibrium diagram and show an eutectic of lead with a lead-barium compound (presumably $Pb_3Ba$) at the composition of 4.5 percent barium and 95.5 per-

cent lead. The barium-lead alloys containing less than this amount of barium have a structure showing this eutectic to-

FIG. 7. CAST SPECIMEN.
Barium, 1.39 percent; lead, balance. Same specimen as in Fig. 6. Etched with 2 percent $HNO_3$ in $C_2H_5OH$. Showing dendrites (crystallites) of lead surrounded by the eutectic between lead and $PB_3Ba$. (x 50).

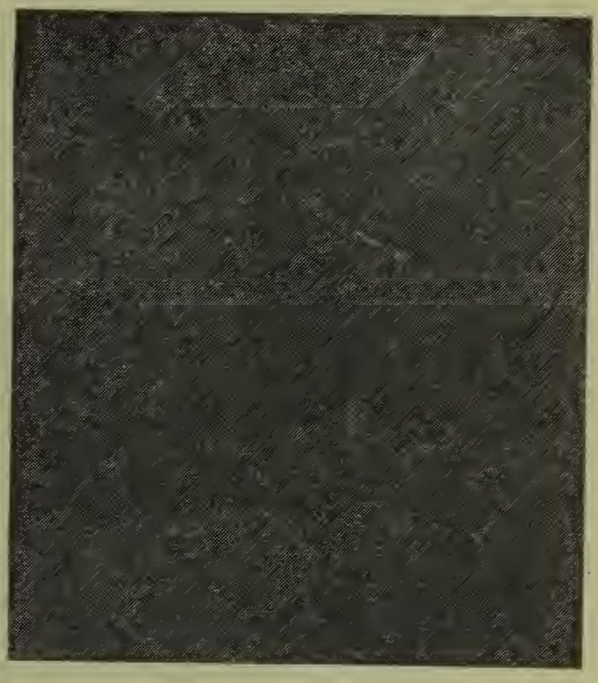


FIG. 8. SLOWLY COOLED.
Barium, 4.65 percent; lead, balance. Polished but not etched; a few rod-like crystals of lead-barium compound ($Pb_3Ba$) in relief. (x 50).

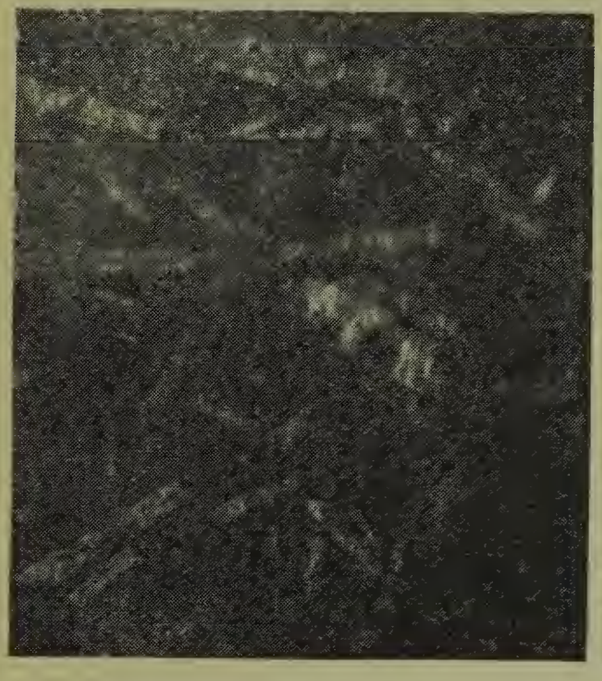


FIG. 9. SLOWLY COOLED.
Barium, 5.5 percent; lead, balance. Similar to Fig. 8, but showing more crystals of $Pb_3Ba$. (x 50).

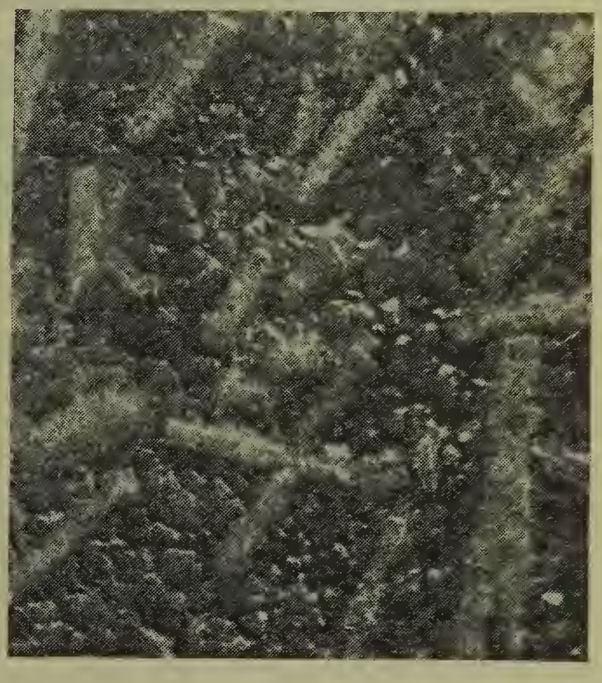


FIG. 10. SLOWLY COOLED.
Barium, 5.5 percent; lead, balance. Same specimen as in Fig. 9. Etched with dilute $AgNO_3$ sol. Showing coarse rod-like crystals of $Pb_3Ba$ in a ground-mass of the eutectic. (x 50).

gether with an excess of lead varying in amounts according to the composition of the alloy. From the diagram published in the article referred to, it appears that an examination was made of an alloy containing as little as 0.14 percent barium, and that presence of eutectic was found therein. Judging from this, no solid solutions are formed unless with smaller amounts of barium. In the work carried out at this laboratory microscopic examination indicates the presence of eutectic in the alloys containing barium

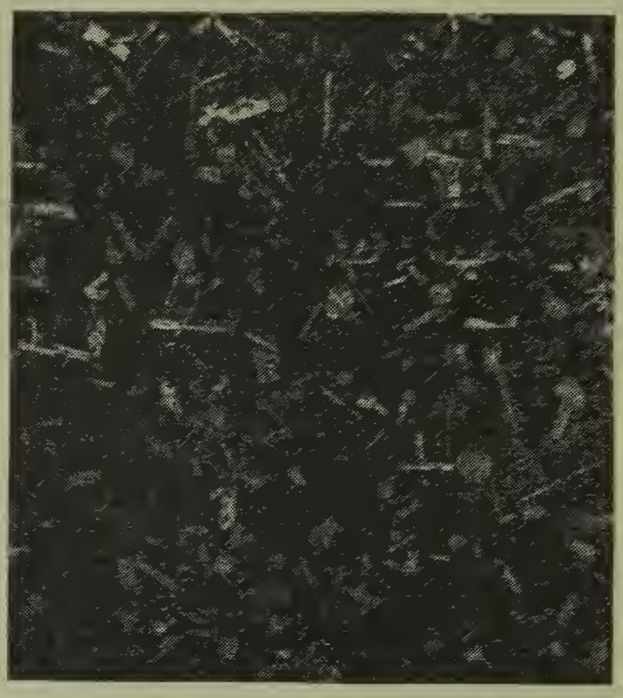


FIG. 11. CAST SPECIMEN.
Barium, 6.05 percent, lead-balance. Similar to Fig. 9. (x 50).

down to at least 0.50 percent (Figs. 5 and 7). In the thermal study the alloy lowest in barium, of which cooling curve was made, namely 0.70 percent barium, plainly shows the presence of eutectic. In the photomicrographs the structure is not sufficiently magnified to show the actual laminations of the eutectic, but the structure is not the completely homogeneous solid solution, rather being composed of homogeneous crystallites (either pure lead or solid solution with a very small amount of barium) surrounded at their boundaries by another component-eutectic. In the alloys containing above 4.5 and up to 6 percent barium, coarse rod-like crystals make their appearance in the micrographs, which presumably consist of the compound $Pb_3Ba$. Figs. 8-11.

In the ternary calcium-barium-lead alloy, containing slight amounts of other elements (Frary metal), the eutectic forms at a slightly lower temperature than is the case with the straight binary barium-lead eutectic. That is, from study of the photomicrographs and thermal equilibrium of Frary metal the eutectic is found to be at a temperature of 284°C. instead of 291°C.; otherwise, however, the structure is such as would be expected from a combination of the binary alloys, calcium-lead and barium-lead. There are, however, some indications of solid solu-

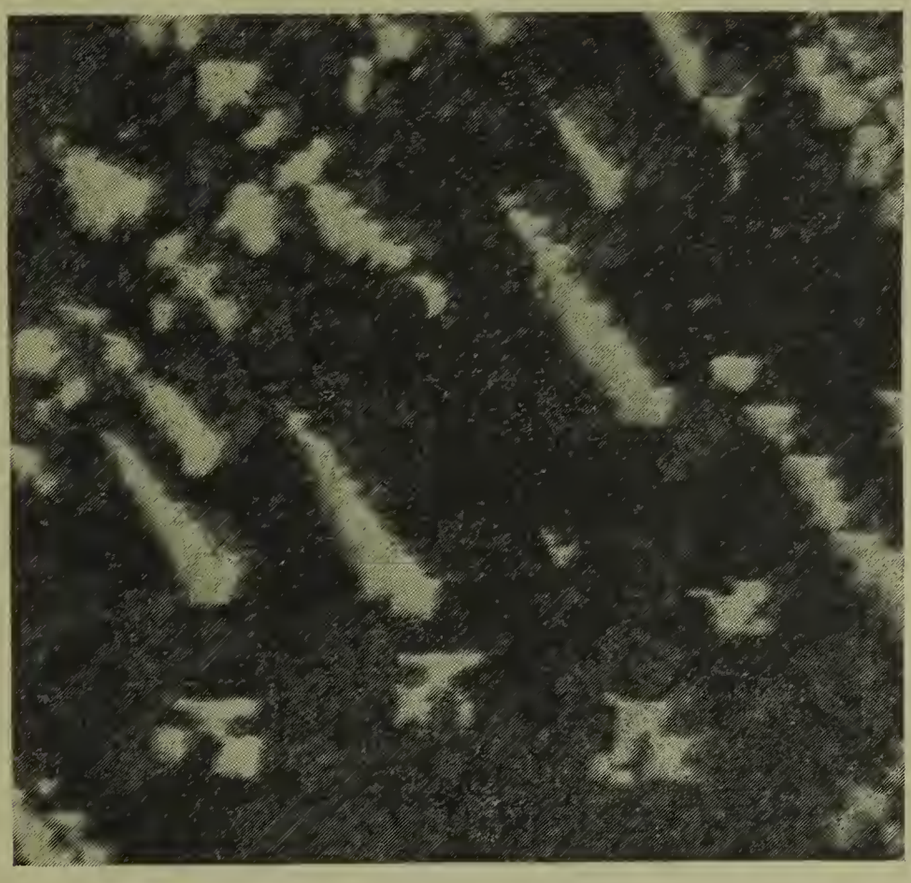


FIG. 12. FRARY METAL.
Top of slowly cooled specimen. Etched with $HNO_3$ and picric acid, showing white crystals of $Pb_3Ca$ and gray areas of Pb (or solid solution), surrounded by dark areas of eutectic. (x 250).

tions being formed in the alloy up to about 0.2 percent calcium and 0.4 percent barium. The structure consists of homogeneous grains of lead, probably containing some calcium and barium in solid solution, surrounded by eutectic of this solid solution with lead-barium compound ($Pb_3Ba$), together with crystals of lead-calcium compound ($Pb_3Ca$) embedded in this ground mass of solid solution and eutectic, Fig. 12. The critical points found in

TABLE II.

*Critical Thermal Points in Calcium-Barium-Lead Alloys.*

| Alloy | | | | Complete Liquefaction Point °C. | Point at which most of the metal freezes °C. | Complete Solidification Point °C. |
|---|---|---|---|---|---|---|
| Barium Percent | Calcium Percent | Mercury Percent | Lead | | | |
| 1.20 | .... | .... | balance | 317 | 317 | 291 |
| .... | 0.80 | .... | balance | 440 | 327 | 327 |
| 1.20 | 0.80 | .... | balance | 446 | 316 | 284 |
| 1.20 | 0.80 | 0.25 | balance | 445 | 314 | 280 |

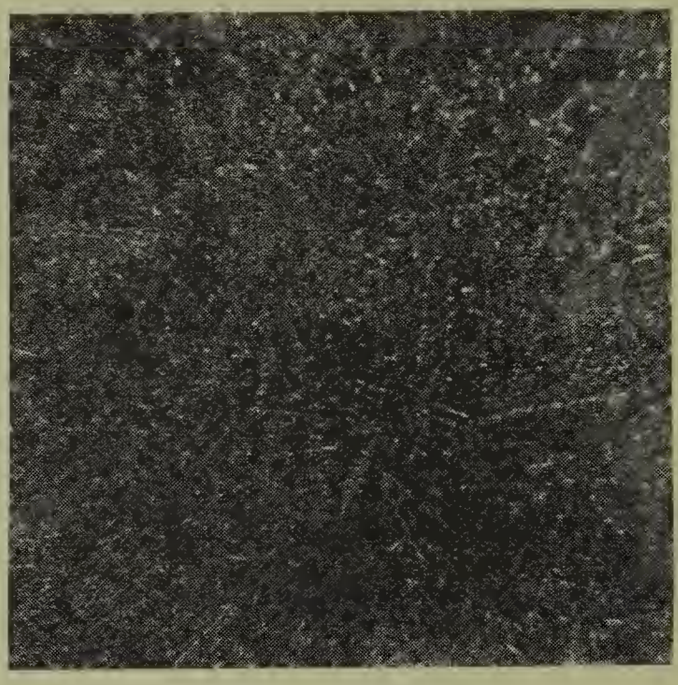


FIG. 13. CAST FRARY METAL.
Polished but not etched. Showing $Pb_3Ca$ crystals in relief, in a ground mass of Pb and Pb-$Pb_3Ba$ eutectic. (x 50).

thermal study of some of these alloys are given in Table II, and photomicrographs are shown in Figs. 12-13.

## CHARACTERISTICS SHOWN IN REMELTING AND CASTING.

As indicated by the above table, there is a range of temperature in cooling such an alloy from a molten state, through which freezing of some of its components continues until complete solidification is reached. The binary barium-lead alloys, in the range studied, melt at a lower temperature and have greater apparent fluidity than pure lead. In the binary calcium-lead

alloys, the complete solidification point is at the melting point of lead, but the presence of lead-calcium compound gives a somewhat higher complete liquefaction point. In the ternary alloy the latter point is above the melting point of lead, while the solidification point is lower than that of lead. This range of temperature through which solidification takes place in Frary metal is no greater, however, than the range of temperature through which most tin base bearing metals are partly fluid and partly solid. For instance, tin base babbitt metals containing up to 8⅓ percent copper have a range of temperature through which a tin-copper compound continues to solidify in a way similar to that in which the lead-calcium compound solidifies in Frary metal.

The practical pouring temperature of any metal should, of course, be well above its complete liquefaction point; the best temperature logically depending upon the size, shape and temperature of the mold into which it is to be cast. Other lead base alloys of the class of bearing metals and type metals melt at a comparatively low temperature, corresponding closely to the melting point of antimony-lead eutectic, and there is in most of these alloys only a short range of temperature between their complete solidification and liquefaction points; whereas Frary metal begins to melt at a temperature closer to the melting point of lead itself and corresponds in its comparatively wide melting range of temperature more nearly to tin base babbitt metals. In remelting and pouring into castings, therefore, it is necessary to use a higher temperature than with lead base alloys containing antimony. Comparing the tendency of these alloys to oxidize, it is simply that which would be expected from the differences in temperature at which they are held in remelting. That is, combination of oxygen in general takes place the more readily the higher the melting temperature. Frary metal does not oxidize or form dross to any greater extent than is found with lead itself or other similar alloys at the temperature in question. In remelting ingots or other cast shapes of any metal or alloy, to avoid oxidation or drossing the crucible, pot or ladle should, when practicable, be first heated to a temperature above the melting point of the metal, a small part of it first melted, and then the balance added a little at a time at the rate at which it melts. That is, a cold melting pot should not be loaded with small cast-

ings and heat afterwards applied for melting. With some alloys there may be a tendency under certain conditions for one element to oxidize more readily than another. However, Frary metal, as now produced, shows no tendency towards loss of its constituent elements by oxidation, when remelted by ordinary good practice. The alloys containing only barium and lead, on remelting, tend to lose barium by oxidation. The calcium-lead alloys as made in this laboratory with the purchased metallic calcium, analysis of which is shown above, do not act in this way. Although calcium itself oxidizes very readily in the atmosphere, there is no tendency of loss of calcium by oxidation in the calcium-lead alloys which we have made. The surface of the molten metal has a very bright silvery appearance, free from oxide. The cause

TABLE III.

*Increase of Hardness with Age.*

| No. | Alloy Composition in Percent | | | | Brinell Hardness Numbers Age of Specimen | | |
|---|---|---|---|---|---|---|---|
| | Barium | Calcium | Mercury | Lead | 1 hr. | 7 days | 28 days |
| 155 | 2.00 | 0.77 | .. | Balance | 25.7 | 29.2 | 31.5 |
| 157 | 1.20 | 0.77 | .. | Balance | 17.6 | 26.1 | 28.4 |
| 159 | 0.40 | 0.77 | .. | Balance | 13.8 | 21.8 | 24.5 |
| 219 | 1.00 | 0.50 | .. | Balance | 18.7 | 22.2 | 23.5 |
| 218 | 1.00 | 0.50 | 0.2 | Balance | 22.6 | 24.4 | 24.7 |

for this may be in the presence, as an impurity in the metallic calcium used, of a very slight amount of some other element. The absence of any tendency in Frary metal to lose its constituent elements by oxidation is probably due to a similar protective or deoxidizing action. The addition of small amounts of some metallic elements has proved beneficial, whereas, the presence of slight amounts of other elements is harmful and must be avoided.

## PECULIAR PROPERTIES.

In the work done on the many experimental alloys prepared, some peculiar characteristics have been noted. Cast specimens of some of the alloys have shown a remarkable increase in hardness and strength upon aging. The cause of this change which takes

place in the solid metal may be similar to the theory advanced for a somewhat like hardening which takes place in duralumin[14]. This is more pronounced with the alloys containing the lower percentages of calcium and barium. The period over which the change in hardness takes place is shortened by the addition of some other elements. The hardness of the alloy, when in certain forms, can be increased by heat treatment. In this respect, also its behavior is similar to that of duralumin.[15] Pure lead, as is well known, emits a very dull sound when struck, while these alloys are quite remarkably resonant. This appears to be largely due to the presence of barium, since we have shown that cast lead containing only 0.08 percent barium is quite highly sonorous, emitting a clear bell-like sound on being struck.

TABLE IV.

*Increase of Hardness by Heat Treatment.*

| Specimen | Brinell Hardness Numbers | |
|---|---|---|
| | Before heat treatment | After heat treatment |
| ½ inch extruded rod | 15.0 | 29.6 |
| 9/16 inch O. D., 5/16 I. D. extruded pipe | 11.2 | 25.0 |
| Sheet | 14.4 | 25.3 |
| Swaged metal | 12.3 | 23.5 |

USES OF FRARY METAL.

Frary metal as described above has a very large field of usefulness, especially as an excellent bearing metal. It has been found valuable for many purposes where strength and hardness is required, and can be readily cast in brass or iron molds, or made into die castings. It has also found use in the form of extruded pipe, tubing and rod; rolled sheets; and in swaged forms. As a bearing metal it has superior qualities and has shown exceptional worth both in tests and in service. It replaces not only lead base but also tin base babbitt metals, and even to some extent bearing bronzes. It has strength without brittleness, and

[14] "The Heat Treatment of Duralumin," by P. D. Merica, R. G. Waltenberg and H. Scott. A. I. M. E., June, 1919.

[15] *Loc. cit.*

also remarkable anti-frictional properties, retaining largely the characteristics of lead in respect to plasticity (malleability, unctuousness).

It is generally recognized that the structure which renders an alloy suitable for use as a bearing metal consists of a crystalline component imbedded in a plastic ground mass. The purpose of this desired structure is to give sufficient hardness to the bearing metal to enable it to resist the required pressure, and at the same time impart to it the quality of plasticity, so that the bearing will adapt itself to any irregularities in fit and alignment. The metal should have the greatest hardness compatible with the necessary

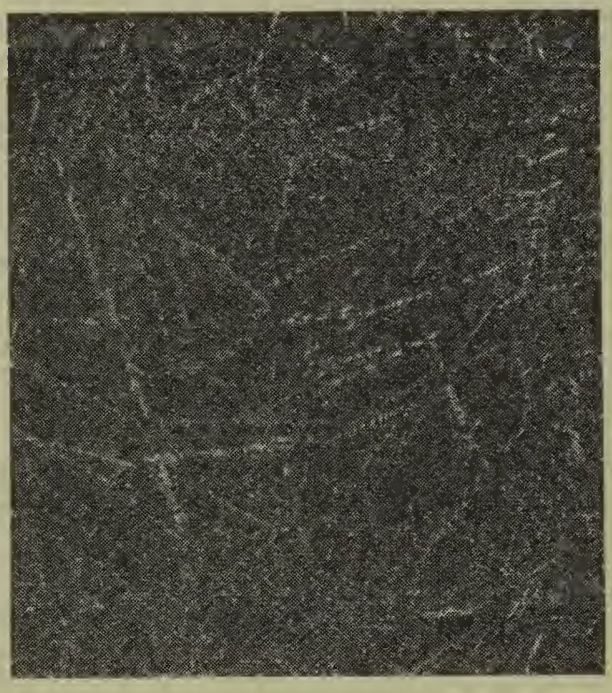


FIG. 14
Cast babbitt metal (88.9 Sn, 7.4 Sb, 3.7 percent Cu). Etched with 2 percent $HNO_3$ in $C_2H_5OH$. Showing crystals of Cu Sn in relief in a ground mass of Sn containing Sb in solid solution (x 50).

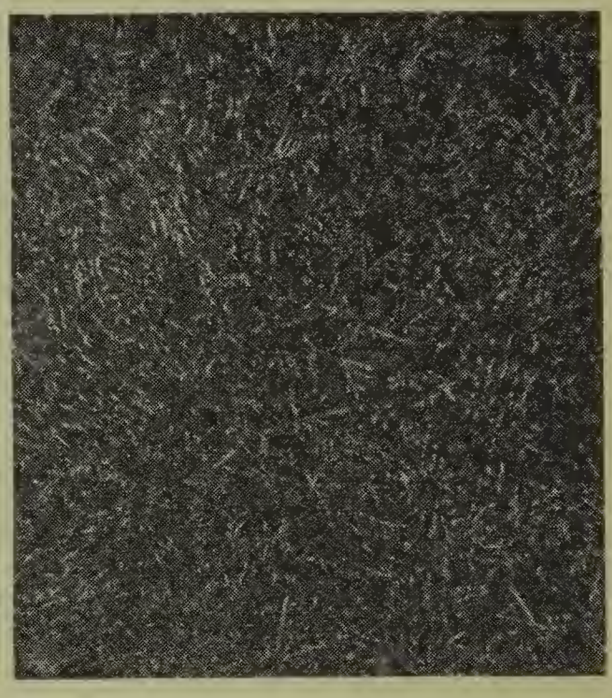
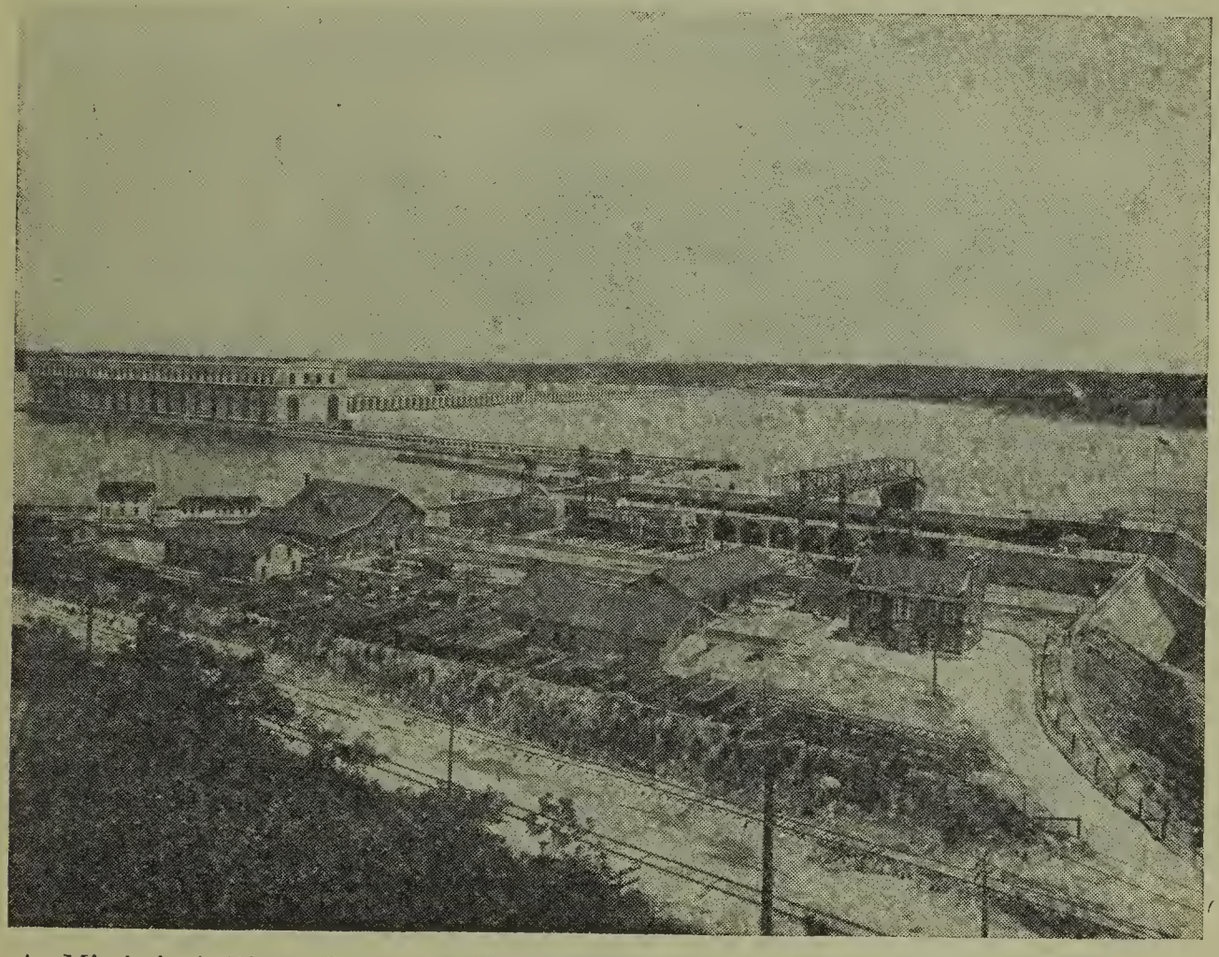


FIG. 15
Cast babbitt metal (85 Sn, 7.5 Sb, 7.5 percent Cu). Similar to Fig. 14, but showing more Cu Sn. (x 50).

plasticity; this hardness, however, being much less than the hardness of the shaft so that in case of injury the latter will not be scored, but the bearing metal itself will suffer. The strength must be sufficient to resist the maximum load to be applied when distributed on approximately the full area designed as bearing surface, but the metal should be sufficiently plastic to flow and smooth out, if, in case of any irregularities in fit or alignment, the load should be carried on too small a part of the bearing surface. A metal having these properties of hardness combined with plas-

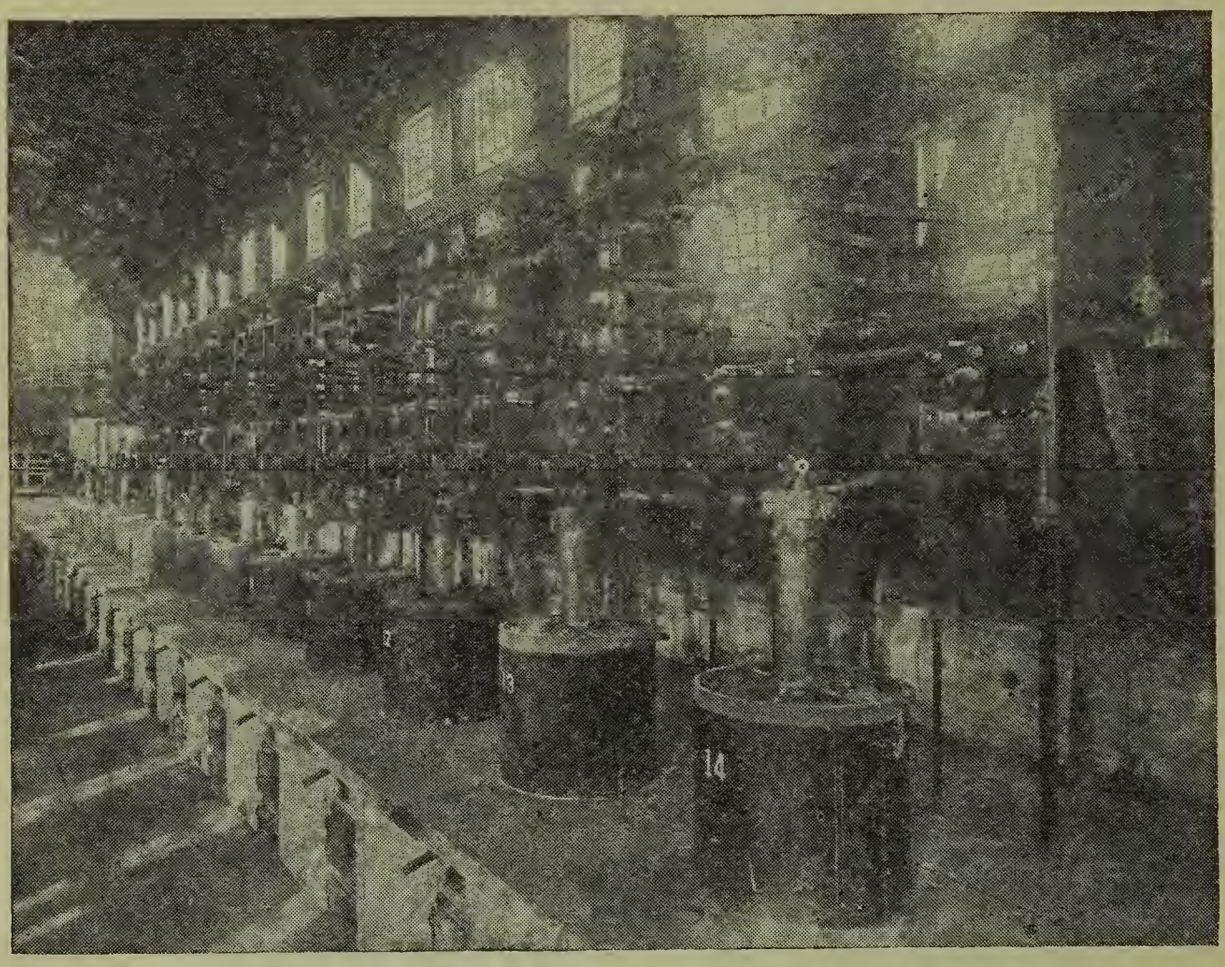
ticity will have good anti-frictional qualities, since, as generally thought of, this term probably involves a low coefficient of friction, and also so-called unctuousness. The former is actually the lower with the greater hardness, and the latter, used in this connection, may be simply the property of plasticity. It appears from photomicrographs and from the working qualities of Frary metal that its structural components have all of these characteristics in a marked degree. Figs. 13-15 show photomicrographs of Frary metal, and two tin base babbitt metals of the composition given, all prepared under the same conditions. These indicate



A. Mississippi River Dam and Hydro-electric Power Plant at Keokuk, Iowa, supplying 100,000 H.P. to surrounding district, including St. Louis.

that the structure of Frary metal is very similar to that of high-grade tin base bearing metals, and the similarity is even more notable when compared with the somewhat different structure of other lead base bearing metals. The Frary metal and the two tin base alloys all have a structure composed of fine interlaced crystals, which have first solidified, imbedded in a matrix or ground mass of the remaining metal. These fine crystals which appear in the structure of Frary metal consist of the compound

$Pb_3Ca$, while the ground mass is composed of a mixture of barium-lead eutectic and an excess of lead, all as described above. In the case of the two tin base alloys, the crystals are composed of a compound of tin and copper, and the ground mass is a solid solution of tin and antimony. In Frary metal the presence of lead (or solid solution of lead with small amounts of calcium and barium) in the ground mass is undoubtedly partly

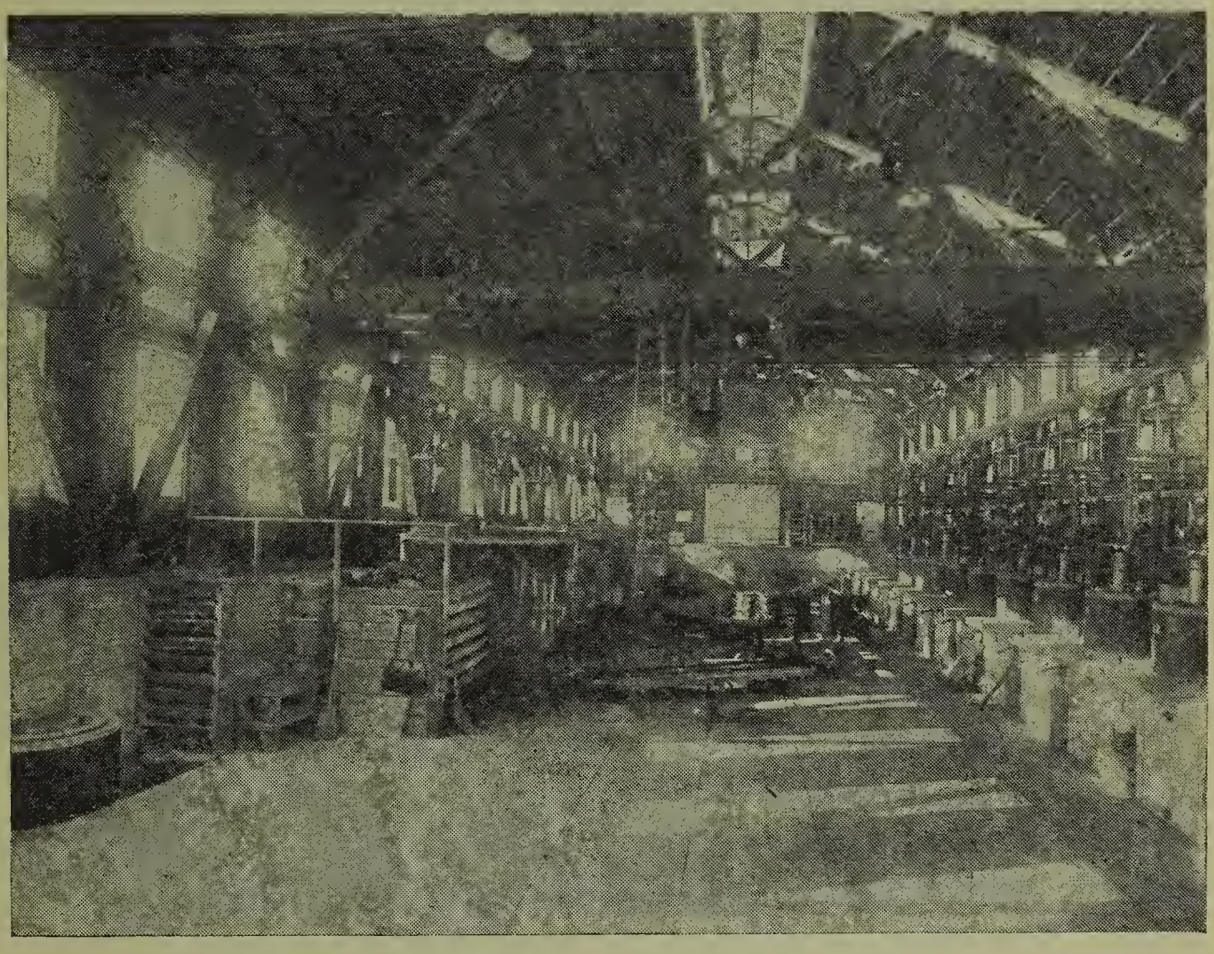


B. United Lead Company, Frary Metal Plant, Keokuk, Iowa. Battery of electrolytic pots.

the cause of the high degree of plasticity which is characteristic of the metal, and it is evidently distributed throughout the alloy in such a way as to result in no sacrifice of hardness. All of this gives to Frary metal the desirable structural characteristics required in bearing metals.

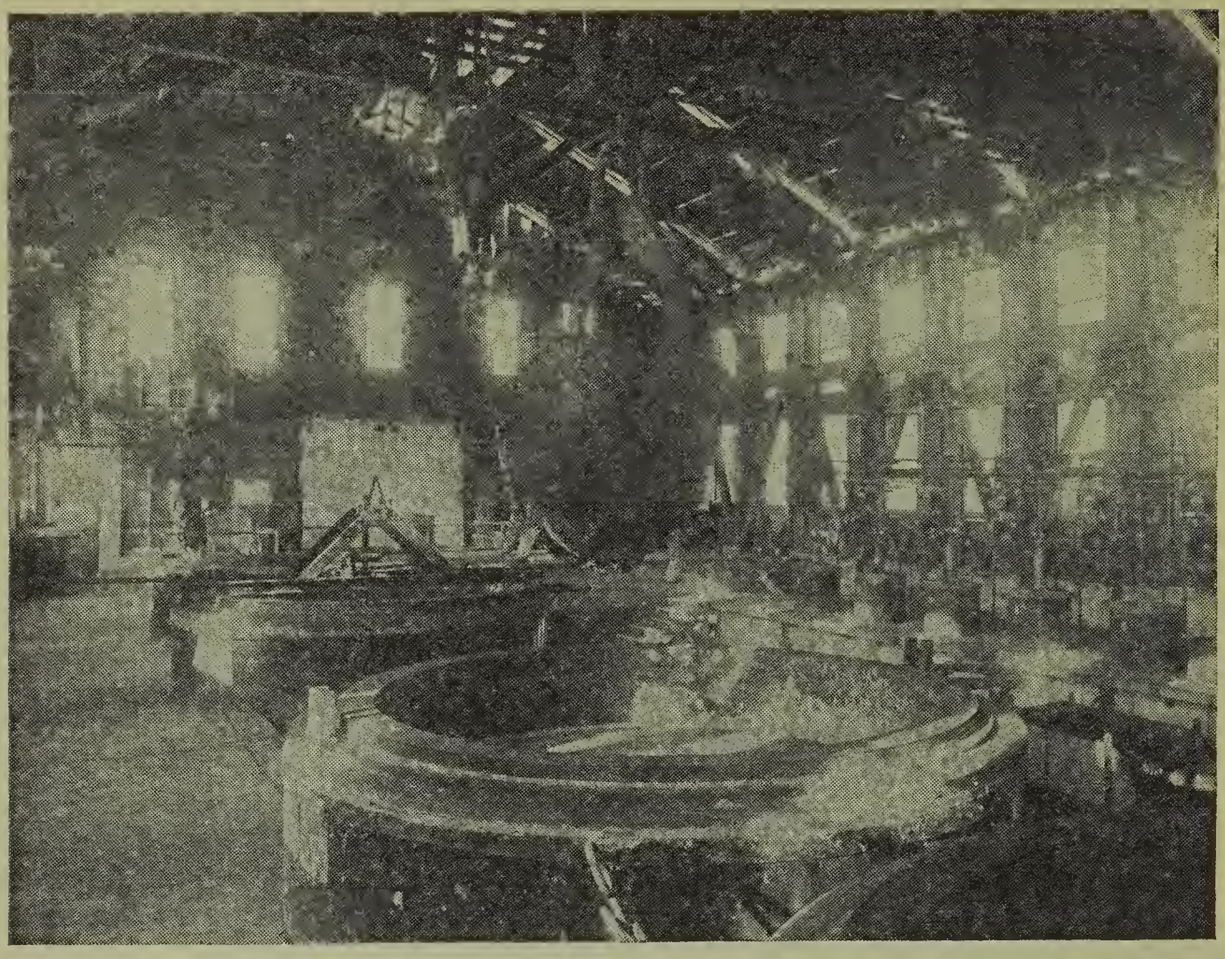
Frary metal possesses a quality of special advantage for service in bearings, in the property of maintaining its hardness and strength at elevated temperatures to a greater extent than do other bearing metals, either lead base or tin base. In actual service bearings attain a temperature above normal, and in many

cases, due to faulty lubrication or other causes, they are run at unusually elevated temperatures. Their value in service then depends upon their properties at such temperatures, although these are usually tested and compared at ordinary room temperature. Metals in general decrease in hardness and strength with rise in temperature, and these properties can be said to have zero value at the respective melting points. The decrease appears in general to be approximately a linear function with change of

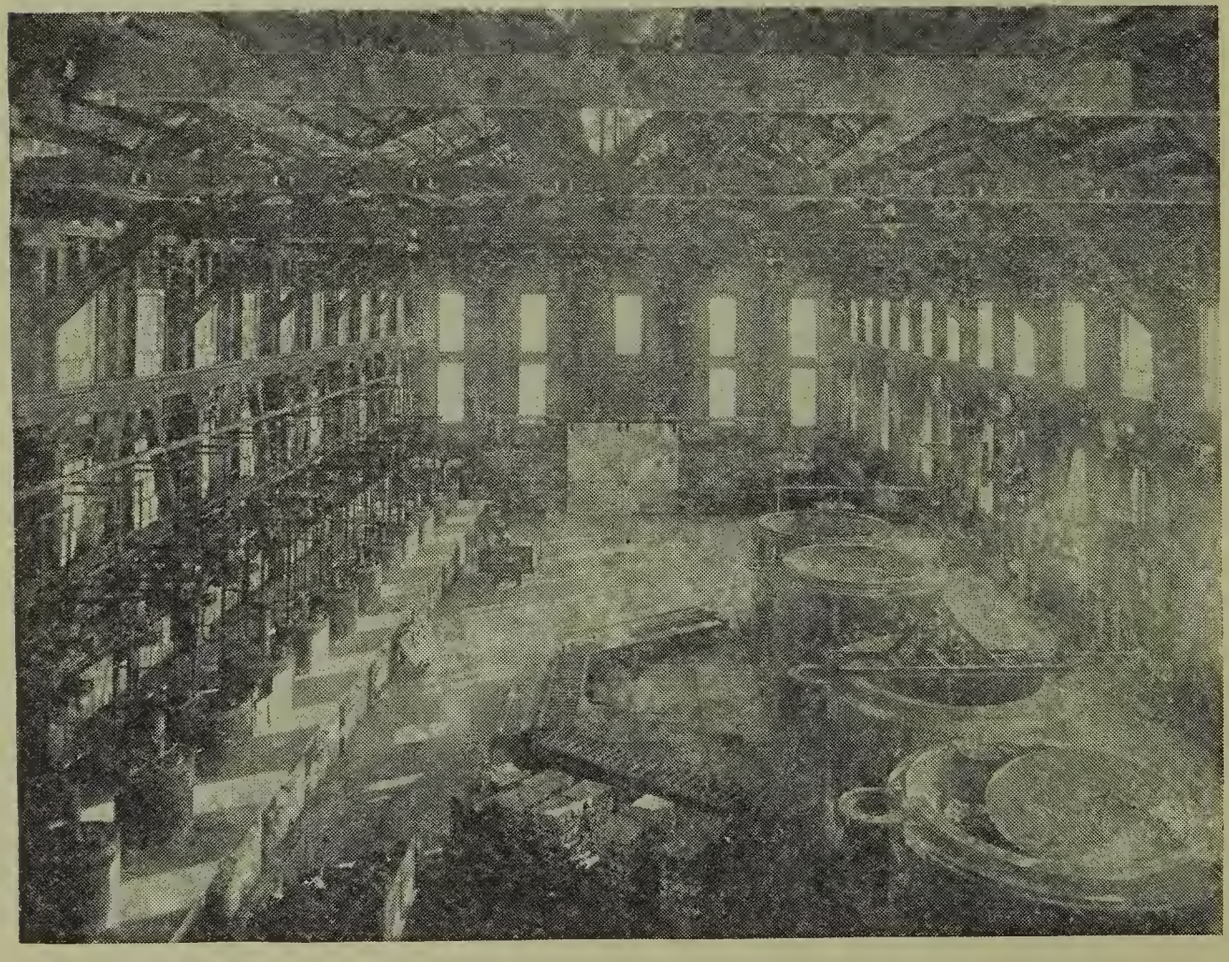


C. United Lead Company, Frary Metal Plant, Keokuk, Iowa. General view of interior.

temperature; therefore, at elevated temperatures, metals having low initial melting points (solidification points) are at a disadvantage in this respect. At the temperature which bearings attain in service Frary metal is harder and has greater compressive strength than other bearing metals, resulting partly from the fact that it has a higher melting point. This is shown by two series of tests carried out at this laboratory, the results of which are recorded in Table V.



D. United Lead Company, Frary Metal Plant, Keokuk, Iowa. Mixing kettles and carrying ladle.



E. United Lead Company, Frary Metal Plant, Keokuk, Iowa. General view of interior. Showing water cooled ingot moulds.

This property of Frary metal of decreasing in strength with rise in temperature to a less extent than other bearing metals, is also shown by compression tests at elevated temperatures made by the Bureau of Standards on Society of Automotive Engineers standard bearing metals,[16] as compared with similar tests made on Frary metal by the Bureau under the same conditions.[17]

A very extensive investigation of Frary metal was made by the Naval Engineering Experiment Station, Annapolis, Md., and reported to the Bureau of Engineering under Test No. 1101, May 14, 1921. The report shows very favorable results obtained with Frary metal, in comparison with navy standard babbitt metal, and also shows that its compressive strength does not fall off so rapidly with rise of temperature.

The writers are indebted to Mr. Thomas F. Wettstein, Manager, United Lead Company, Keokuk plant, for his suggestions

TABLE V.

*Hardness of Bearing Metals at Working Temperatures.*

| Alloys | Percent | | | | Brinell Hardness Nos. | |
|---|---|---|---|---|---|---|
| | Lead | Tin | Antimony | Copper | 20°C. | 100°C. |
| 1..... | .. | 91 | 4.5 | 4.5 | 24 | 12 |
| 2..... | .. | 88.9 | 7.4 | 3.7 | 28 | 14.5 |
| 3..... | .. | 85 | 7.5 | 7.5 | 31 | 16 |
| 4..... | 10 | 75 | 12 | 3 | 29.5 | 13 |
| 5..... | 48 | 40 | 10 | 2 | 21 | 9 |
| 6..... | 77 | 10 | 12.5 | 0.5 | 25 | 13 |
| 7..... | 80 | 5 | 15 | .. | 22.5 | 10.5 |
| Frary metal .. | 97.5 | .. | .. | .. | 27.5 | 18 |

*Brinell Hardness Numbers at Elevated Temperatures.*

| | 25°C. | 50°C. | 100°C. | 150°C. |
|---|---|---|---|---|
| Genuine Babbitt ..... { Sn 88.9 percent, Sb 7.4 percent, Cu 3.7 percent } | 28.3 | 23.5 | 13. 8 | 9.0 |
| Frary Metal.... 29181 | 29.6 | 27.2 | 20.9 | 14.0 |

[16] "Some Properties of White Metal Bearing Alloys at Elevated Temperatures," by John R. Freeman, Jr.. and R. W. Woodward; Bureau of Standards. Abstracted in Metal Industry, **19**, 68.

[17] "Bureau of Standards Report on Compression Tests of Frary Metal at Elevated Temperatures," to National Lead Company, March 24, 1921.

relating to description of the process of manufacture, and also for kindly furnishing for this article the photographs A to E of the Mississippi River Dam, and of the plant where Frary metal is manufactured.

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## DISCUSSION.

C. H. PROCTOR[1]: I would like to ask whether a combination of the barium could be used as a purging factor for antimonial lead in the use of commercial antimonial alloys? The only way we can purge the metal as we use it now is by the poling method, by using green hickory wood poles. Considerable dross is frequently included in the commercial metals as we purchase them, and quite frequently some arsenic still remains in the metals. Of course, in casting in moulds, etc., we often find segregation spots, that are due largely to some arsenious lead. Would the combination as proposed in your paper be of any value in purging this metal if added in minute proportions?

G. O. HIERS: I am not prepared to state as to that; we have not made any experiments along those lines.

C. H. PROCTOR: It would be interesting; there is so much art metal work that is cast from antimonial lead and a great deal of electroplating of antimonial lead castings. At present there is considerable difficulty owing to segregated spots and dross, so that it is almost impossible to get the metal in proper condition. We accomplish a good deal by using the green hickory method of poling to bring the dross to the surface; I was wondering whether the combination outlined by you could be used to any advantage?

G. O. HIERS: We have made no experiments along those lines, but on antimony-lead alloys we often add some phosphor-tin.

C. H. PROCTOR: I meant 80 percent lead, 12 percent antimony, just the commercial by-product of the antimony and lead.

[1] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.

J. W. RICHARDS[2]: I would like to ask Mr. Hiers about how large a current is used on those pots which are referred to here?

G. O. HIERS: The potential difference between the electrodes is 10 volts for each pot with a current of 2,000 amperes.

J. W. RICHARDS: I once discussed this with Mr. Coho, and he gave me some data; I have forgotten the amount of current; about 2,000 amperes. There is considerable chance for increase of efficiency in getting barium and strontium into the metals. If it takes 2,000 amperes and takes three days to get a 2 percent alloy with two tons of lead in there, the efficiency must be somewhere in the neighborhood of 20 percent, or not more than that, counting on the calcium alone, and on the barium less than 20 percent efficiency; so I think there is considerable room for increasing the efficiency by a study of the conditions.

C. G. SCHLUEDERBERG[3]: I would like to ask the author whether this alloy has been adopted commercially by any of the companies using bearing metal? Is it widely used?

G. O. HIERS: Yes, it has a wide use. We hope some day to use it on all the freight cars to replace the old bronze bearing, but owing to the ownership of the freight cars and the way the bearings are repaired, it is a difficult proposition for us to get the business that way. However, we have used these bearings on many trolley lines, such as interurban lines. We have a large field in using the metal as a washer, and for use in linings, die castings and bearings.

[2] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

[3] Asst. to Manager, Supply Dept., Westinghouse Elec. & Mfg. Co., E. Pittsburgh, Pa.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# ELECTROLYTIC CORROSION OF LEAD-THALLIUM ALLOYS.[1]

By Colin G. Fink[2] and Charles H. Eldridge.[3]

Abstract.

Various lead alloys were investigated with the object of making a lead base anode that would resist the corrosive action of an acid copper sulfate solution containing nitric and hydrochloric acids. A minimum corrosion loss of 1.2 lb., per 100 lb. of Cu deposited, resulted with a lead anode containing 10 percent Tl and 20 percent Sn, as compared with a 65 lb. loss for ordinary lead. The authors find that in general alloys with high melting points are more resistant to corrosion. [A. D. S.]

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During the past few years a series of experimental lead alloy anodes were made and tested in the Research Laboratories of the Chile Exploration Company. The object of the investigation was to make a lead base anode which would be insoluble in the electrolyte used in the tank house at Chuquicamata, Chile. The research also covered the suitability of lead alloys for acid pump fittings. Of the various lead alloys investigated we have selected for this paper the lead-thallium alloys,[4] not so much on account of their commercial importance as on account of their scientific interest.

At present ferrosilicon anodes are used at Chuquicamata. These anodes are brittle, call for electric smelting furnaces and corrode away at the rate of 5 to 6 lb. per 100 lb. of copper deposited. The percentage of iron in the electrolyte tends to increase and, as is well known, the presence of iron in quantity in a copper electrolyte has a marked depressing effect on the current

[1] Manuscript received, August 30. 1921.

[2] Consulting Electrometallurgist, New York City.

[3] Metallurgical Engineer, South Yonkers, N. Y.

[4] U. S. patent No. 1384056, July 12, 1921.

efficiency. Now, a lead alloy has many inherent qualities that make it promising as an anode material. For example, a lead alloy anode is (a) malleable and can easily be drilled, machined and hammered, giving a good busbar connection; (b) can be melted in a low temperature (low cost) furnace and cast at low temperatures into any desired shape; (c) since very thin plates can be cast it will occupy a minimum of space in the tanks; (d) has a very constant low voltage of about 2 (at a current density of 20 amp./sq. ft. or 2.2 amp/sq. dm.) through a wide range of electrolyte composition and alloy composition as against 2.5 to 3.0 volts for 13 percent ferrosilicon.

## THE WORKING HYPOTHESIS.

In the alloys here recorded, the reason for selecting thallium as an addition to lead was because we thought it might serve as a valuable non-corrosive constituent on account of its unusual behavior towards oxygen. This property we had investigated some ten years ago in connection with the research on "getters" or salts introduced into the tungsten lamp to eliminate or reduce blackening of the inner walls of the bulb. There are two oxides of thallium, $Tl_2O_3$ and $Tl_2O$, and, contrary to the usual behavior of metal oxides, the *lower* thallium oxide is the more stable. Our assumption was that thallium as anode material might form the higher oxide due to reactions with the anions at the anode surface, and that the higher oxide would break down to form the lower oxide plus oxygen gas, thus bringing about a freer liberation of oxygen at the anode than is possible with most metals.

G. Grube and A. Hermann[5] found it impossible to oxidize thallosulfate to thallisulfate by bubbling oxygen gas through an acid sulfate electrolyte. On the other hand, they found that thallisulfate decomposed slowly at ordinary temperatures, but that the presence of small amounts of a catalyst, such as platinum, brought about an almost spontaneous decomposition of the thalli salt into the thallo salt. Similarly, light catalyzed the reduction of the higher sulfate.

[5] Zeitsch. für Electrochemie, 1920, 26. 291.

W. J. Mueller[6] investigated the behavior of thallium in sulfuric acid solutions, and found that at voltages below 4.8 the metal goes into solution as monovalent ions. However, early investigations of the oxide film formed anodically on thallium metal have shown rather conclusively that this is composed chiefly of thallic oxide, $Tl_2O_3$.[7] Foerster interpreted the formation of this higher oxide on the surface of the anode as the result of the hydrolytic decomposition of thallic sulfate, $Tl_2(SO_4)_3$.[8] Edgar F. Smith in his "Electroanalysis" cites Heiberg's method of precipitating quantitatively $Tl_2O_3$ on the anode from acid sulfate solutions of thallium.[9]

Under oxidizing conditions, the film of thallic oxide adheres to the surface very tenaciously. On the other hand, as Boettger had shown as early as 1863, the oxide can be reduced and the metal dissolved in ethyl and methyl alcohol.[10]

As regards the solubility of thallium metal in the various acids present in our electrolyte numerous investigations have been made. The electrolyte at Chuquicamata contains small amounts of nitric and hydrochloric acids, and it is the presence of these constituents that causes the rapid corrosion of ordinary lead anodes, which are giving such satisfactory service at Ajo in the straight sulfate electrolyte. In our electrolyte the lead loss amounts to 65 lb. per 100 lb. of copper deposited. We give below the relative solubilities in grams per litre of the sulfates, chlorides and nitrates as taken from Seidell. Although too much dependence as a positive guide cannot be placed on the relative solubilities of the sulfates, chlorides and nitrates of the various metallic constituents that enter into the composition of our alloys—and there are a number of cases known where the solubility of the alloy is decidedly greater than that of any of its constituents—yet these solubilities have some bearing and importance when one or the other metal is present in excess in the alloy or exists as such in

[6] *Ibid,* 1909, **15**, 696.

[7] Sir Wm. Crookes, Chem. News, 1861, **3**, 193, 303; 1863, **7**, 290; Lamy, *Compt rend,* 1862, **54**, 1255.

[8] Zeitsch. für Elektrochemie, 1897, **2**, 653.

[9] Heiberg, Z. anorgan. Chem., 1903, **35**, 347; see also A. R. Foster and E. F. Smith, Journ. Amer. Chem. Soc., 1899, **21**, 936.

[10] Boettger, Journ. für prakt. Chem., 1863, **90**, 27; Margarete Bose, Z. anorgan. Chem., **35**, 347; *ibid,* 1905, **44**, 237.

the interfaces. Naturally, too, we ought to take into account the solubilities of complex salts which are undoubtedly formed under our conditions.

| | Sulfate | Chloride | Nitrate |
|---|---|---|---|
| Lead | 9.941 | 10.8 | 565.0 |
| Thallium | 48.700 | 3.4 | 95.5 |

These values hold good only in the absence of complex formation. The solubility of ordinary lead anodes in our electrolyte we attribute largely to the presence of nitric acid. The low solubility of thallium nitrate was an additional reason for adding thallium to the lead.

Finally, the exceptional shape of the lead-thallium fusion curve as compared with most other binary lead alloy curves encouraged us to believe that unusual solubility results would be forthcoming.

### SIZE OF ANODES.

The experimental anodes were cast into shapes 5 inches (12.7 cm.) long by 1 inch (2.5 cm.) wide by 0.25 inch (0.6 cm.) thick. Graphite molds were used.

### COMPOSITION OF ELECTROLYTE.

The composition of the electrolyte at the beginning of a test run was as follows (grams per liter): Cu 55, Fe 8, $HNO_3$, 10, Ca 1, Mg 6, $H_2SO_4$ 20, Cl 1, Na 24, K 6, Al 1.5, total sulfate ($SO_4$) 152 g.

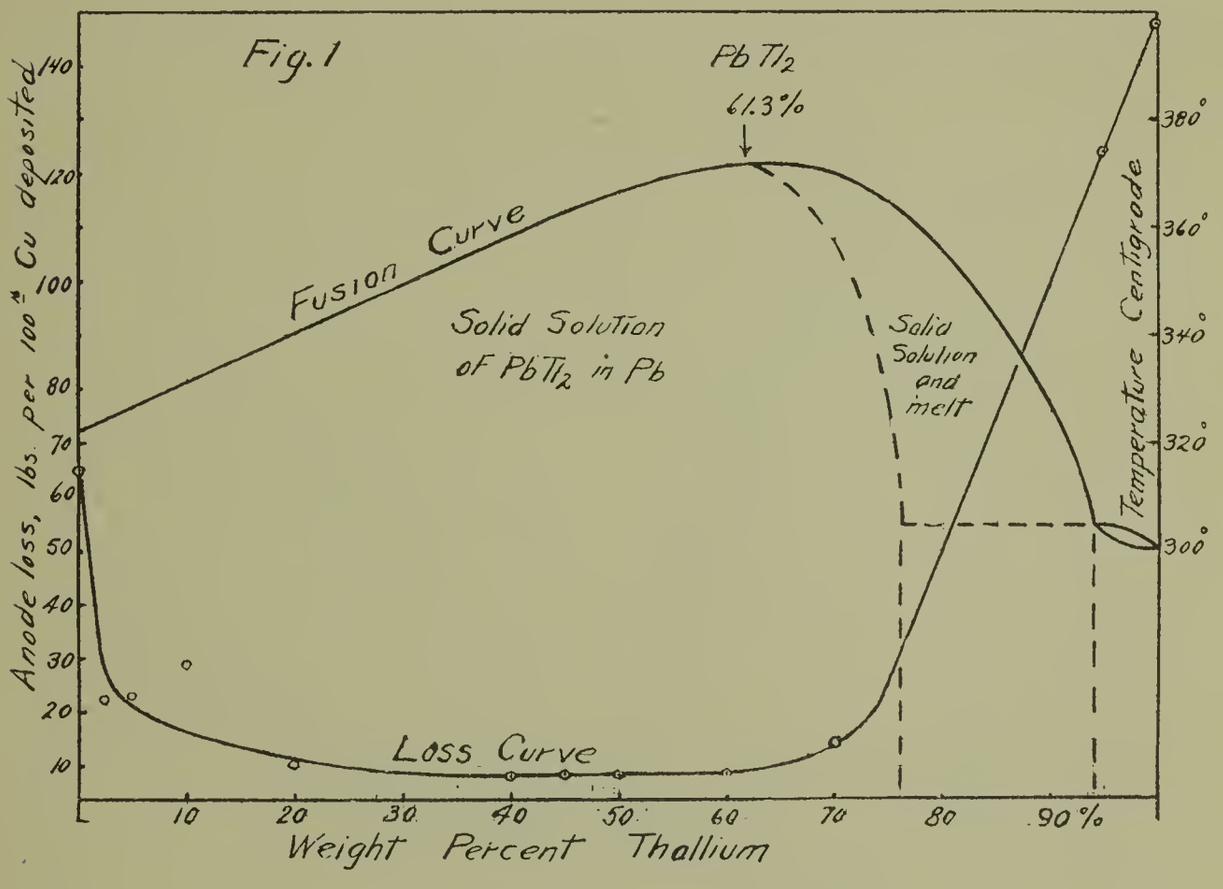
### TEST CONDITIONS.

The alloy anodes were suspended in the electrolyte contained in individual cells connected in series with a cell having a 13 percent ferro-silicon anode and a copper coulometer. The temperature was room temperature and varied $\pm$ 5° C. A copper sheet cathode was suspended on either side of each anode at a distance of 1.5 inches (3.8 cm.) between centers. The current density was 20 amp./sq. ft. (2.2 amp./sq. dm.) of anode. Electrolysis was continued until the copper concentration dropped to 15 grams per litre. The electrolyte was then regenerated by adding enough copper carbonate to restore the copper concentration to 55 grams per litre and to neutralize at the same time the excess acid formed. The test was then continued. A complete run averaged 21 days.

Many promising anodes were given second runs lasting 54 days. By carefully weighing the anodes before and after the test the corrosion per 100 lb. of copper deposited was determined.

### THE BINARY ALLOYS: LEAD-THALLIUM.

A series of twelve alloys was tested ranging from ordinary lead to thallium metal. The results are startling. Ordinary lead gives a corrosion loss of 65 lb. per 100 lb. of Cu deposited. The addition of only 2 to 3 percent of thallium to the lead immediately



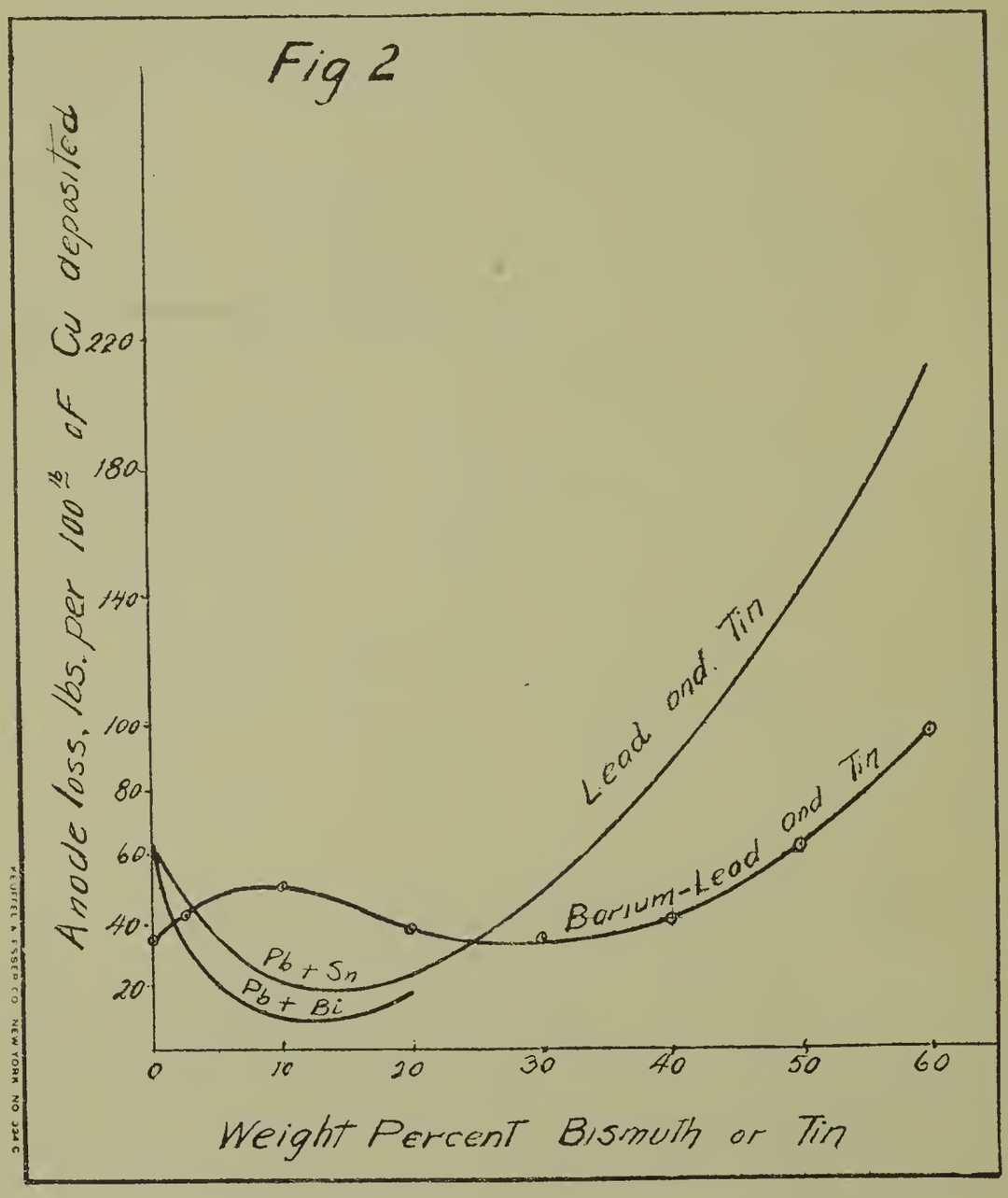

decreases the anode loss, until at 40 percent thallium we have a minimum loss of only 8 lb. Fig. 1 shows the loss curve plotted along with the fusion curve.[11] The loss curve has a flat minimum from about 20 to 60 percent Tl, which is an attractive feature from a commercial point of view on account of ease of duplication. At 40 percent Tl we have an alloy consisting of a half saturated solid solution of $PbTl_2$ in Pb. Note also that the alloys with low melting points have comparatively high corrosion losses. The curve furthermore shows that if there is an excess of thal-

[11] Fusion curve is that of Lewkonja's Z. anorgan. Chem., 1907, **52**, 452; cf. N. S. Kurnakow and N. A. Puschin, *ibid*, 1907, **52**, 430.

lium present above that required to form the compound $PbTl_2$ the solubility rapidly increases.

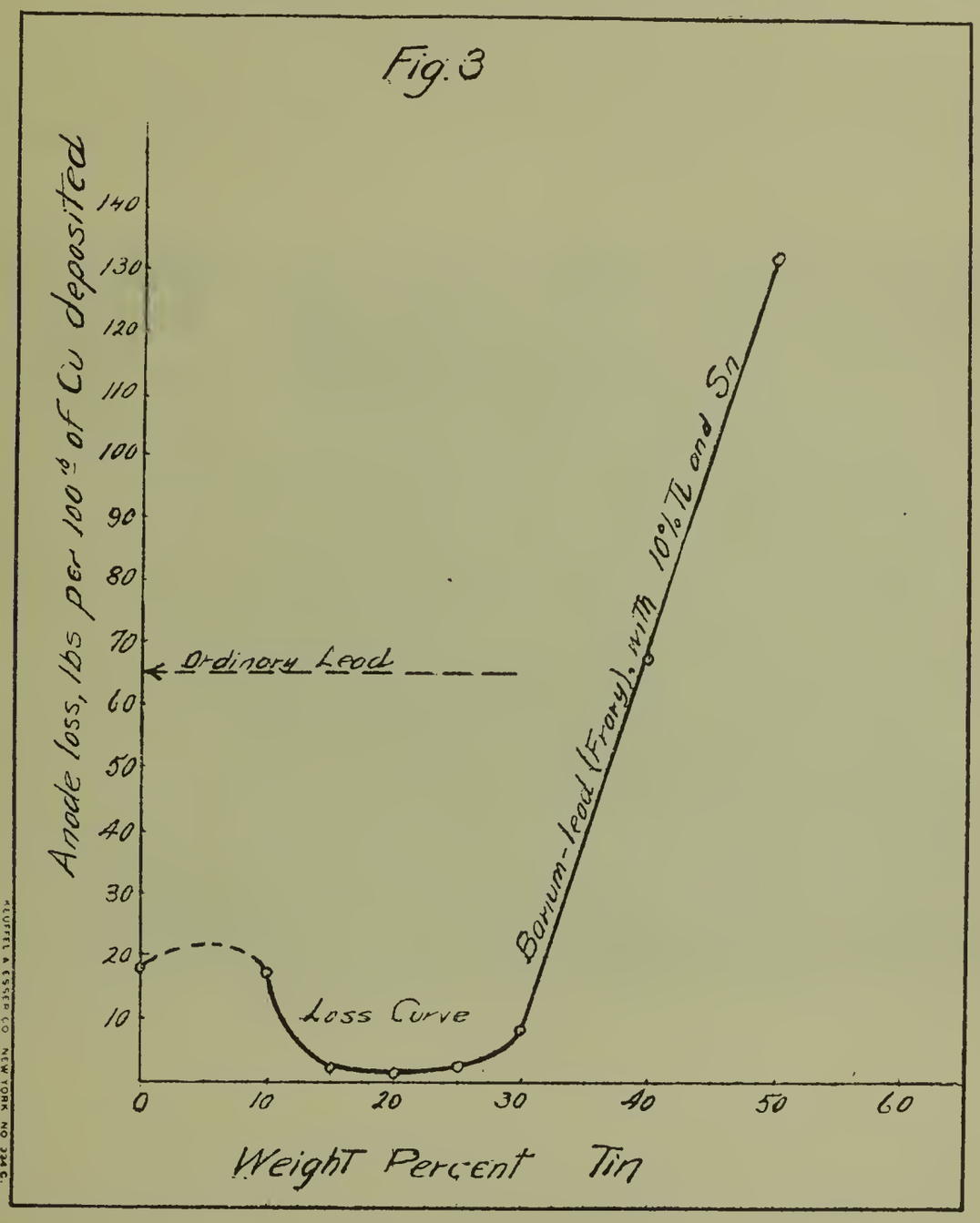
### LEAD-BISMUTH AND LEAD-TIN ALLOYS.

Next a series of lead-bismuth and lead-tin alloys were tried out. The tin and bismuth were selected hoping that they would




counteract the corrosive action of the nitric acid present in our electrolyte. Again the corrosion of the pure lead was rapidly decreased by the addition of either of these metals. Fig. 2 shows the two loss curves. We have sharp minimums at about 12 percent bismuth and at about 15 percent Sn. But the alloys as far as loss goes are far inferior to the lead-thallium alloys indicated in

Fig. 1. The fusion curve of the lead-tin alloys[12] shows an eutectic at 67 percent Sn and the fusion curve for the bismuth-lead alloys[13] shows an eutectic at 56 percent Bi. When we compare these fusion curves with the loss curves respectively, we again find that




in general the resistance to corrosion increases with the melting point.

### TIN-FRARY METAL ALLOYS.

The Frary metal used contained 2 to 3 percent calcium plus barium, balance lead. The Frary metal-tin curve is also shown in

[12] Roberts-Austin, Fourth Report Alloys Research Committee, 1897.
[13] Guertler, Metallographie, 1912.

Fig. 2. The Frary metal alone without tin has a loss of 32 lb. or decidedly lower than that of pure lead. By the addition of calcium + barium we have flattened the sharp minimum found for the simple lead-tin alloys.

### TIN-THALLIUM-FRARY METAL.

With 2 to 3 percent Tl and up to 30 percent Sn the corrosion averaged 30 lb. per 100 lb. of copper deposited, and ranged from

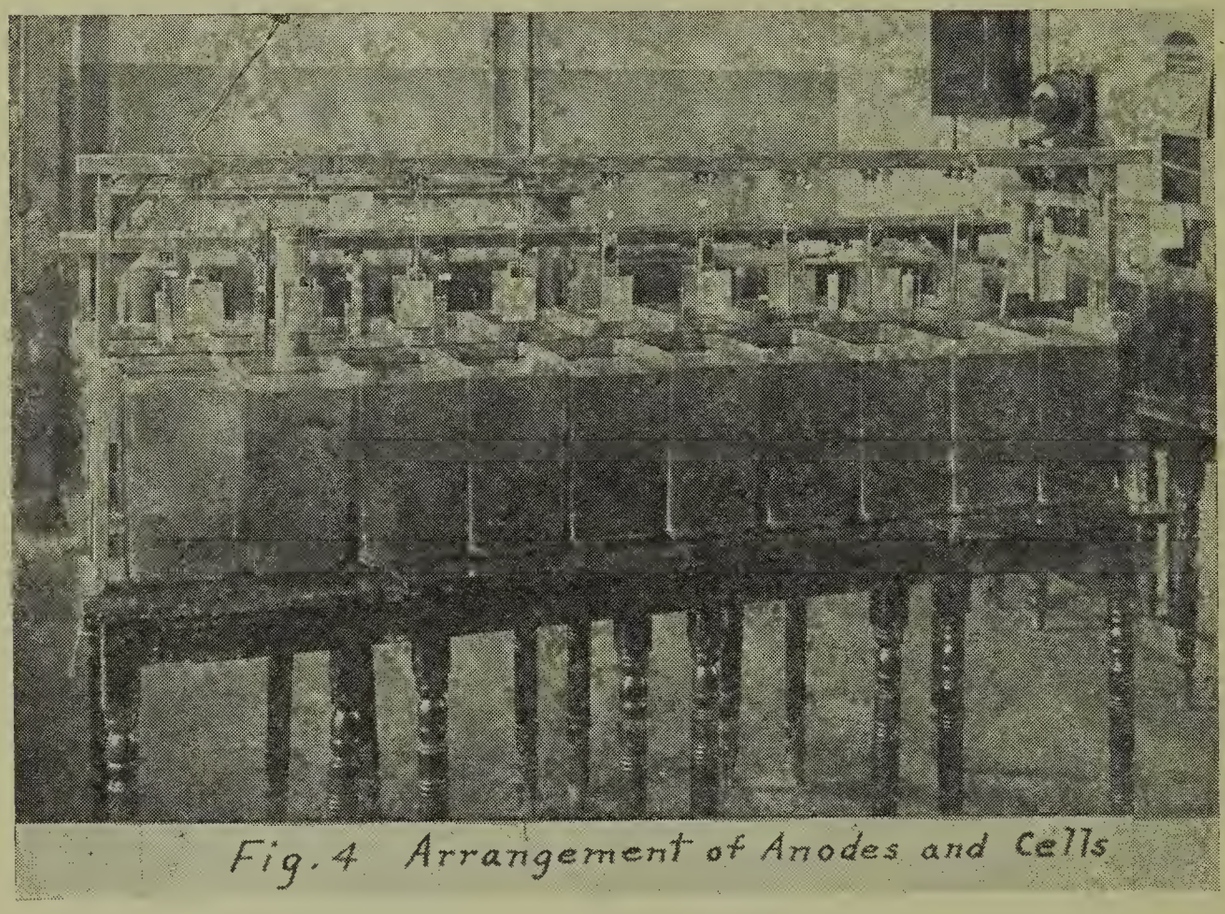


Fig. 4 Arrangement of Anodes and Cells

26 to 43 lb. With 5 percent Tl and up to 30 percent Sn the corrosion averaged 20 lb. and ranged from 15 to 27 lb. With 20 percent Tl and up to 30 percent Sn the corrosion was very constant, ranging from 2.5 to 5 lb. With 10 percent Tl and up to 60 percent Sn we get most gratifying results as shown in the loss curve, Fig. 3. Here we have a smooth curve with a well-defined minimum at about 20 percent Sn. The alloys with 15, 20 and 25 percent Sn show a corrosion loss of but 2.1, 1.2, and 2.6 lb. respectively, as against 65 lb. for ordinary lead. The flat minimum in Fig. 3 has been carefully checked by duplicate alloys and

duplicate tests. Since thallium is the most costly of the various constituents of these alloys, the low thallium alloys are the more promising commercially.

### TIN-THALLIUM-BISMUTH-FRARY METAL.

Bismuth, which forms a very insoluble oxynitrate, as compared to a very soluble lead nitrate, was next added to the lead-tin-thallium alloys. In every case a reduction in corrosion was noted. There was a decided increase in the resistance to corrosion in the very low percentage thallium alloys. This meant a reduction in first cost. For example, an anode consisting of 77 percent Frary metal, 10 percent Sn, and 2-3 percent Tl showed a loss of only 5.5 lb. when bismuth was present to the extent of 10 percent, and a loss of 31 lb. when bismuth was absent.

### OTHER ALLOYS.

Besides the alloys above referred to we investigated the lead-tin-thallium, barium-lead-thallium, barium-lead-tin, barium-lead-tin-manganese, barium-lead-tin-bismuth, barium-lead-tin-bismuth-silver alloys, etc.

As regards hardness and ductility of the lead alloys studied we may say that although harder than ordinary lead, not one was found to be brittle. A few notes regarding the surface films formed during electrolysis may be of interest. Ordinary lead: usually a loosely adherent sulfated film; rarely a brown peroxide film which built up in layers. Frary metal: always a brown peroxide film which built up in layers, porous and non-adherent. Thallium-lead alloys: a closely adhering brown-black film; on many it was exceedingly difficult to remove this film in preparing the anodes for the final weighing. As regards the films on the thallium alloys, we had hoped that the presence of the thallium would promote the rapid formation and evolution of oxygen gas at the anode, so as to reduce to a minimum the oxidation of the ferrous ions. All our current efficiency measurements however tend to show that thallium oxide is no better than lead oxide in this respect. In either case, the efficiencies at room temperature and at anode current densities of 20 amp./sq. ft. (2.2 amp./sq. dm.) were from 75 to 80 percent.

## CONCLUSION.

The addition of thallium to lead alloys has been very effective in reducing anodic corrosion in acid copper sulfate electrolyte containing nitric and hydrochloric acids. The low corrosion losses are largely due to a very adherent film formed during electrolysis.

In conclusion, we desire to acknowledge the many useful suggestions offered by Mr. C. A. Rose and Mr. C. E. Singer, during the carrying out of the above tests.

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## DISCUSSION.

G. O. HIERS[1]: In relation to the peak in the lead-thallium equilibrium diagram, it may be noted that there are also peaks in the lead-calcium equilibrium diagram. In fact, when plotting both curves on the same scale, the lead-calcium peaks (at 650° C. and 1,100° C.) are great in comparison with the lead-thallium peak (at 374° C.). It might, therefore, seem, according to Dr. Fink's scheme of reasoning, as outlined in the discussion of this paper, that the lead-calcium alloys would be superior to the lead-thallium alloys.

COLIN G. FINK: I might say to Mr. Hiers that there is another curve you must take into account, and that is the cost curve; that has a peak too, and with the calcium you soon reach altitudes where you cannot hold your breath any more.

G. B. HOGABOOM[2]: I would like to ask Dr. Fink if he went far enough to know whether it would act in solders?

COLIN G. FINK: It will alloy readily, but you can find solders a whole lot cheaper than lead-thallium. Thallium is $5.00 to $20.00 a pound.

G. B. HOGABOOM: It is not the cheapness, it is the melting point, you increase the melting point by adding thallium; there-

[1] Research Laboratory, National Lead Co., Brooklyn, N. Y.
[2] Research Electroplater, Scovill Mfg. Co., Waterbury, Conn.

fore you would probably get a higher melting point in the solder that would be of value.

COLIN G. FINK: I might add that since soldering is largely an alloying proposition, lead-thallium does alloy readily with brass, if that will answer your question.

G. B. HOGABOOM: I mean to use it for soft soldering, one that can be applied in soft soldering copper; not a fusion solder, just a soft solder.

COLIN G. FINK: We added to the lead-thallium alloy a series of other metals, including copper and silver, and it will alloy readily with these.

G. B. HOGABOOM: Are any of these alloys commercially feasible?

COLIN G. FINK: While developing the lead-thallium alloy anodes we came upon another alloy, which was much cheaper than lead-thallium. The copper refining plant objects to the introduction into the electrolyte of impurities, which may be deposited on the cathode and reduce the electrical conductivity of the copper. In the anode that is being introduced in the Chile plant now I have overcome these objections.

HENRY HOWARD[3]: I would like to ask Dr. Fink if in connection with this work he has found anything that would improve lead chambers, and would be practical from the cost point of view?

COLIN G. FINK: I would like to refer Dr. Howard to the National Lead Company. Frary metal is a good deal better than ordinary lead as regards resisting corrosion of $H_2SO_4$.

[3] Grasselli Chemical Co., Cleveland, O.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# A NEW THEORY OF THE CORROSION OF IRON.[1]

By J. Newton Friend.[2]

Abstract.

After discussing the known facts and theories, and the still unexplained phenomena of rusting, the author puts forward an auto-colloid catalytic theory, which postulates the corrosion as starting by the formation of colloidal ferrous hydroxide. This oxidizes by contact with the air to hydrated ferric hydroxide sol, which latter is alternately reduced by contact with iron and oxidized by contact with air, thus continuing the corrosion, and, upon flocculation, it yields rust. [J. W. R.]

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During the last twenty years numerous observations on the corrosion of iron have been made which cannot be harmonized with any of the existing theories. A few of the more important anomalies are as follows:

1. It is known that dilute solutions (one percent) of alkali carbonates entirely inhibit the corrosion of iron immersed in them. This could readily be explained either by the so-called acid theory, or by Whitney's theory. According to the latter, the alkali carbonate reduces the number of hydrogen ions in the water to such an extent that corrosion cannot take place. According to the acid theory the explanation is similar, although usually expressed somewhat differently. In 1908, however, Heyn and Bauer[3] began to publish the results of a monumental research upon the influence exerted by various salt solutions upon iron, and called attention to the remarkable fact that exceedingly dilute solutions

[1] Manuscript received June 4, 1921.

[2] Municipal Technical School, Birmingham, England.

[3] Heyn and Bauer. Mitt, Königlichen Materialprüfungsamt, Berlin. 1908, 26, 2; 1910, 28, 62.

of the alkali carbonates not only fail to inhibit corrosion, but actually stimulate it. Their results are shown in Fig. 1, the concentrations being expressed logarithmically as abscissae, and the corresponding corrosions, as determined by losses in weight, as ordinates. The increased corrosion is very pronounced, and neither could it be predicted nor can it be explained by any recognized theory of corrosion.

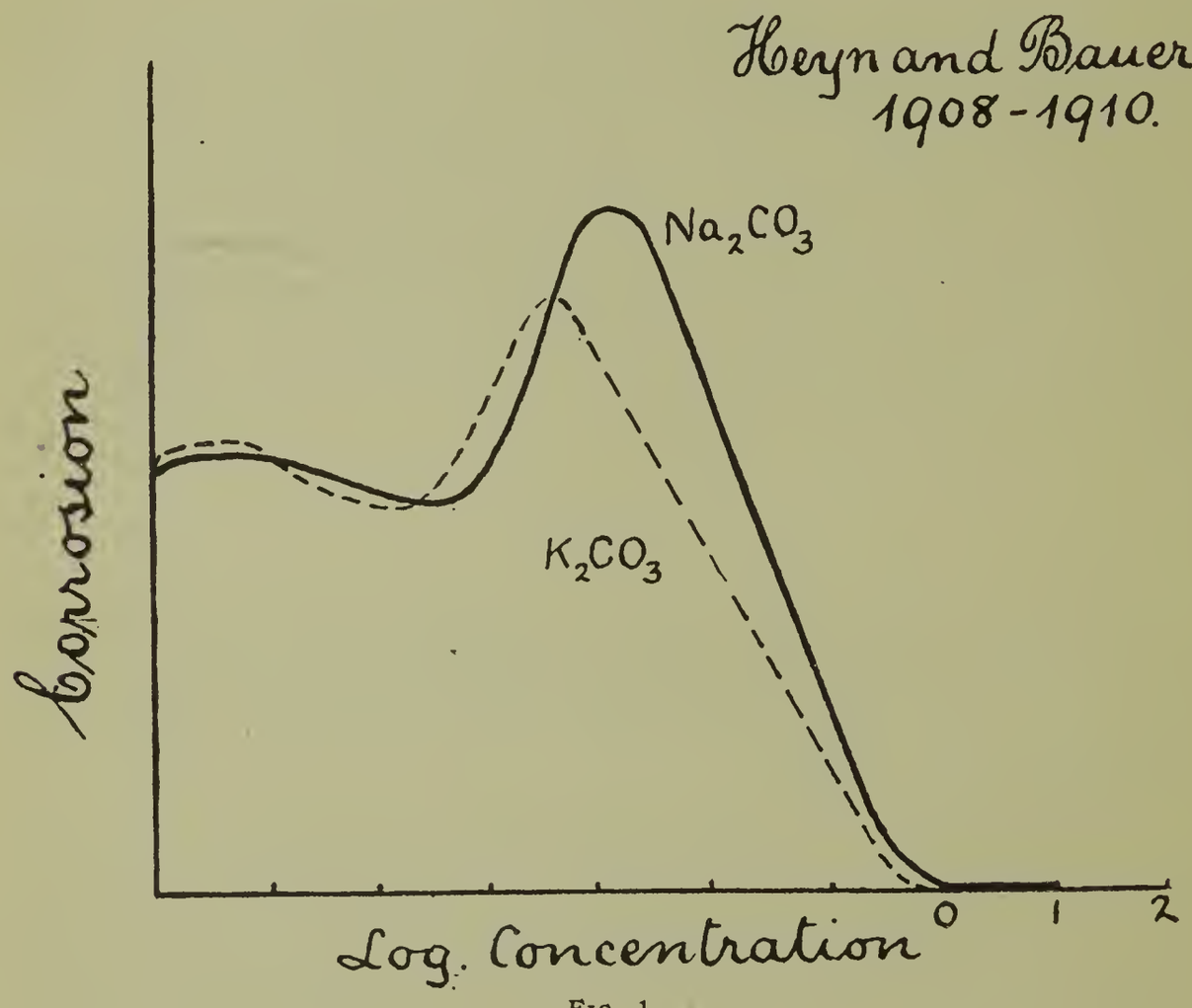


FIG. 1.

2. Dilute solutions of sodium chloride are known to be exceedingly corrosive towards iron. In 1845, however, Adie[4] pointed out that saturated solutions of common salt are actually less corrosive than distilled water. He attributed this to the decreased solubility of oxygen in the solutions, and supported his theory by a few determinations of the solubility of oxygen in different solutions.

Undoubtedly this is correct in so far as it goes, but it cannot

[4]Adie, Min. Proc. Inst. Civil Engineers, 1845, 4, 323.

possibly be the whole explanation. Walker, Cederholm and Bent[5] have shown that the rate of corrosion of iron in water is directly proportional to the partial pressure of the oxygen. Hence, if this is the only factor to be considered in connection with corrosion in inorganic salt solutions, the corrosion curve for various concentrations should exhibit a general similarity to the oxygen solubility curve, after the maximum corrosion has once been attained. Such, however, is not usually the case as is evident from a consideration of the curves in Fig. 2. The continuous line gives the relative corrosions of pure electrolytic iron

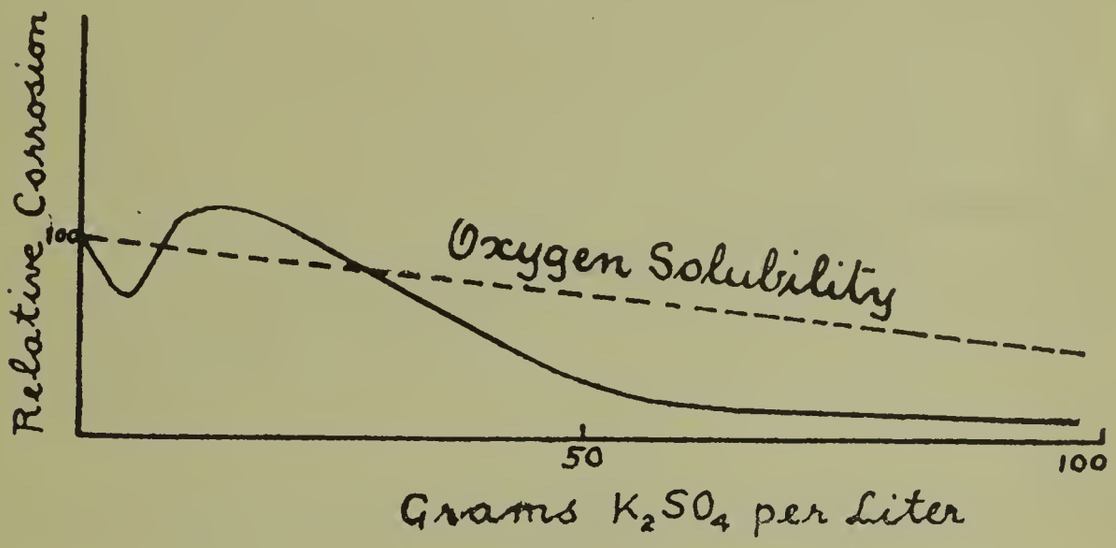


FIG. 2.

foil in various concentrations of potassium sulphate solution at 15° C.,[6] whilst the broken line gives the relative solubilities of oxygen[7] in the solutions. Thus, while the corrosion is reduced from 100 to about 14 in a solution containing 90 grams of potassium sulphate per litre, the solubility of the oxygen has only fallen from 100 to 67. It is interesting to note on the other hand, however, that a similarity between the curves has been found with sodium chloride at 23.5° C.[8] as shown in Fig. 3.

3. An even more remarkable observation has been made[9] in connection with the influence of temperature upon the relative corrosion of iron in sea water and in distilled water. At about

[5] Walker, Cederholm and Bent, J. Amer. Chem. Soc., 1907, **29**, 1251.
[6] Friend and Barnet, J. Iron and Steel Institute, 1915, **1**, 336.
[7] Calculated from the data obtained by MacArthur, J. Physical Chem., 1916, **20**, 495.
[8] Friend and Barnet, J. Iron and Steel Institute, 1915, **1**, 336.
[9] Friend and Brown, J. Chem. Soc., 1911, **99**, 1302.

10° C. sea water is considerably more corrosive than distilled water, also at 10° C.; at room temperature the two are almost equally corrosive; while at 30° C. sea water is appreciably less corrosive than distilled water, also at 30° C. The results may be expressed graphically as in Fig. 4 by taking the observed corrosion in distilled water at each temperature as 100, and expressing the corrosion in sea water relatively thereto.

The question of the oxygen solubility does not enter into this, and no explanation has hitherto been offered for this anomaly. The subject is one of great importance to marine engineers and is deserving of careful attention.

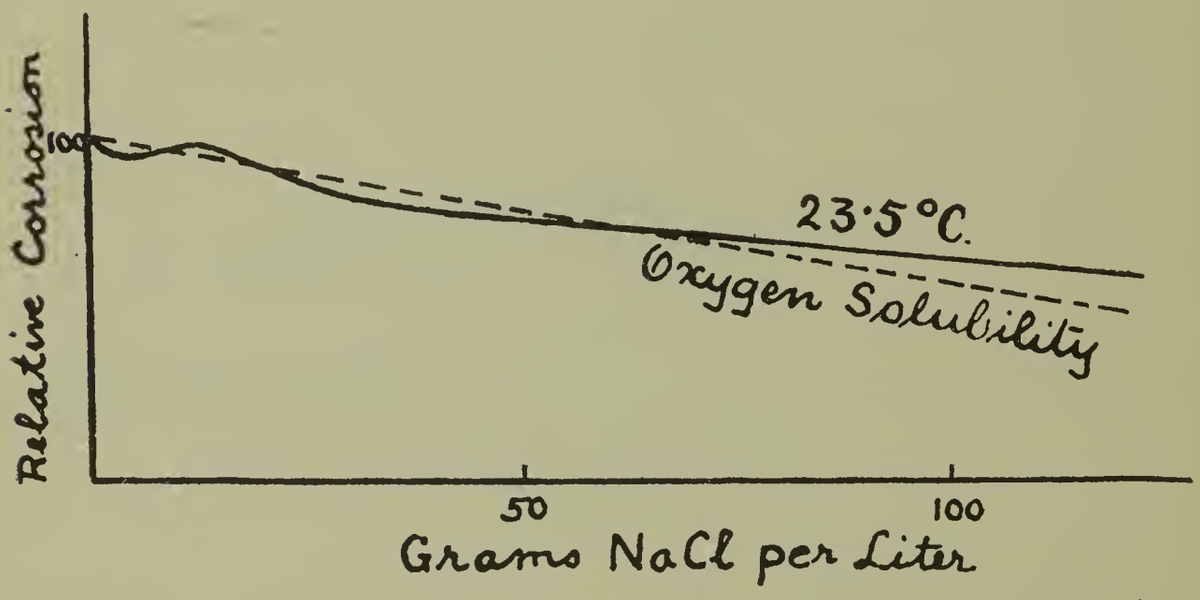


Fig. 3.

4. Iron does not corrode when immersed in pure ethyl alcohol, and, as this substance is not an electrolyte, the addition of alcohol to water would not be expected to influence in any chemical manner the corrosion of iron immersed in the same. Some physical action might, however, result, such, for example, as variation in the oxygen solubility, and the rate of corrosion might thus reasonably be expected to bear a closer relationship to the oxygen solubility curve than in the case of the dissolved salts already considered. A glance at the curves in Fig. 5 shows that such is by no means the case.[10] There does not appear to be the slightest connection between the two curves.

[10] Friend J. Chem. Soc., 1921, **119**, 932.

5. In 1913[11] the author called attention to the curious fact that iron immersed in water for several months corrodes more seriously if protected with a thick layer of paint than with a thin one. Liebreich and Spitzer[12] had already observed a similar phenomenon in a series of acceleration tests in which painted iron plates were kept in boiling water for some hours. These results, so different from what one might expect, and so opposed to those obtained by the author in an extensive series of field tests in which painted iron plates were exposed to atmospheric corrosion for varying periods ranging up to five years,[13] have now been

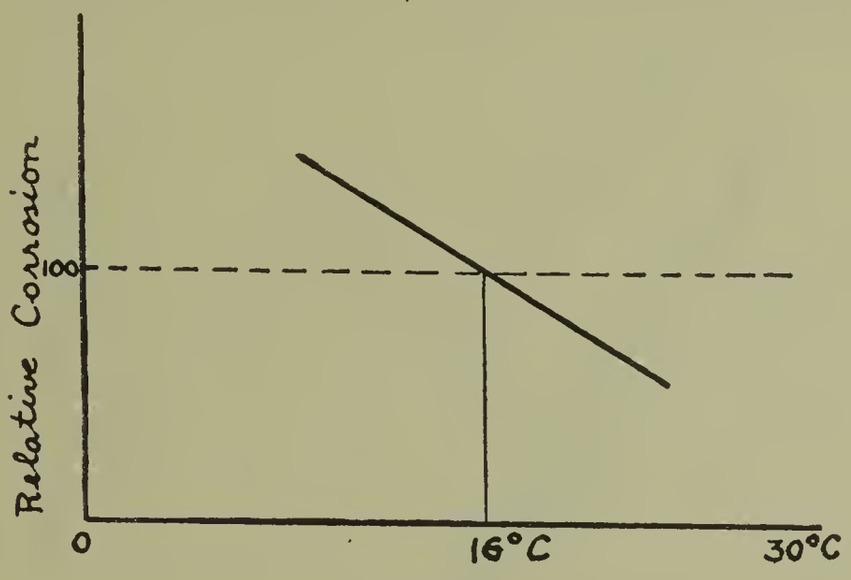


FIG. 4.

confirmed. Full details of the experiments have not as yet received publication, but the curves in Fig. 6 give a good idea of the general type of result obtained. The various paint mixtures used consisted of pure boiled oil with different amounts of deep Indian Red pigment (essentially $Fe_2O_3$) ranging from 30 to 80 percent of pigment. There can be no doubt, therefore, that the observation applies generally for sub-aqueous corrosion, and is not merely a coincidence for one particular mixture.

6. In 1910 Heyn and Bauer [14] showed that, when iron is immersed in flowing water, the rate of corrosion at first rises rapidly with the rate of flow. In the case of a sample of cast iron, a gentle flow increased the rate of corrosion to over 800

[11] Friend, Carnegie Scholarship Memoirs of the Iron and Steel Institute, 1913, **5**, 1.
[12] Liebreich and Spitzer, Zeitsch. Elektrochem., 1912, **18**, 94.
[13] Friend, J. Iron and Steel Institute, 1921, **1**, 365.
[14] Heyn and Bauer, *loc. cit.*

percent of that obtaining in still water. Further increase in the rate of flow, however, caused a diminution in corrosion. The method adopted by these investigators consisted in suspending the metal plates in large beakers and allowing a rapid current of water to flow through from the mains. This scheme, however, does not admit of the attainment of high rates of flow over the surface of the metal, the maximum velocity attained being given as 350 litres per hour, and probably equivalent to about 250 feet per hour.

In order to determine the effect of still higher velocities the author placed narrow, weighed strips of Kahlbaum's pure

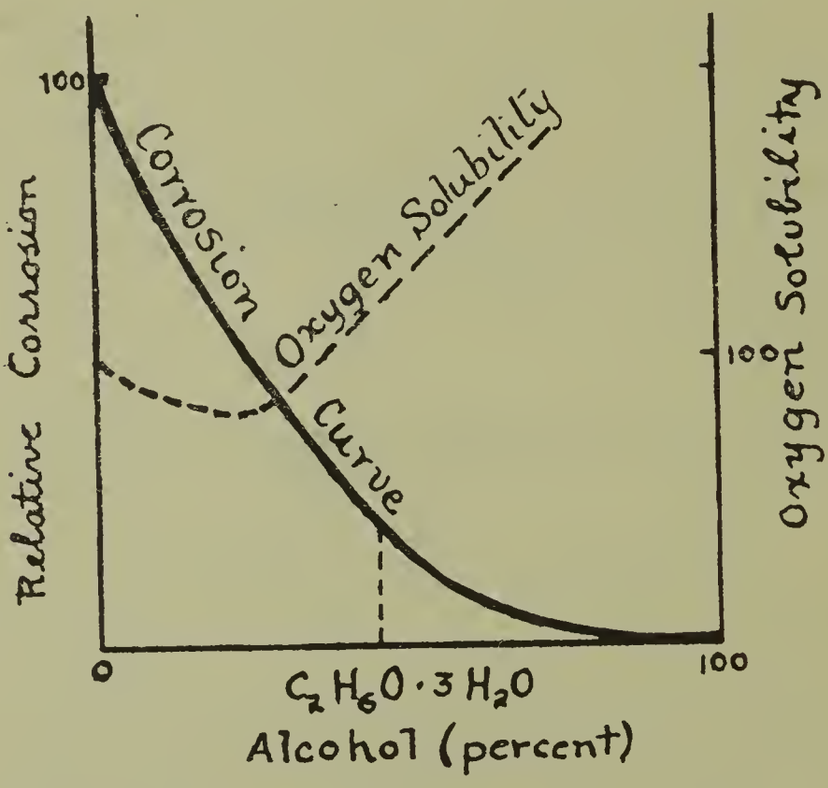


FIG. 5.

electrolytic iron foil in a glass tube, connected with pressure tubing to the main water supply. The strips were kept from being ejected from the tube by the force of the water by means of platinum wire, as shown in Fig. 7. The rate of flow of the water varied from 0 to nearly 6 miles per hour (262 cm./sec.) and the duration of the experiments from one to two days.

The results are shown graphically in Fig. 8. It will be observed that the iron always suffered a slight loss in weight, but that no visible corrosion occurred with velocities

exceeding some 2.5 miles per hour (111 cm./sec.), while the loss in weight was very much less than that in still water. This result appeared very remarkable, for, according to unpublished results of J. H. Dennett, B. Sc., and the author, the rate of solution of iron in acid is almost directly

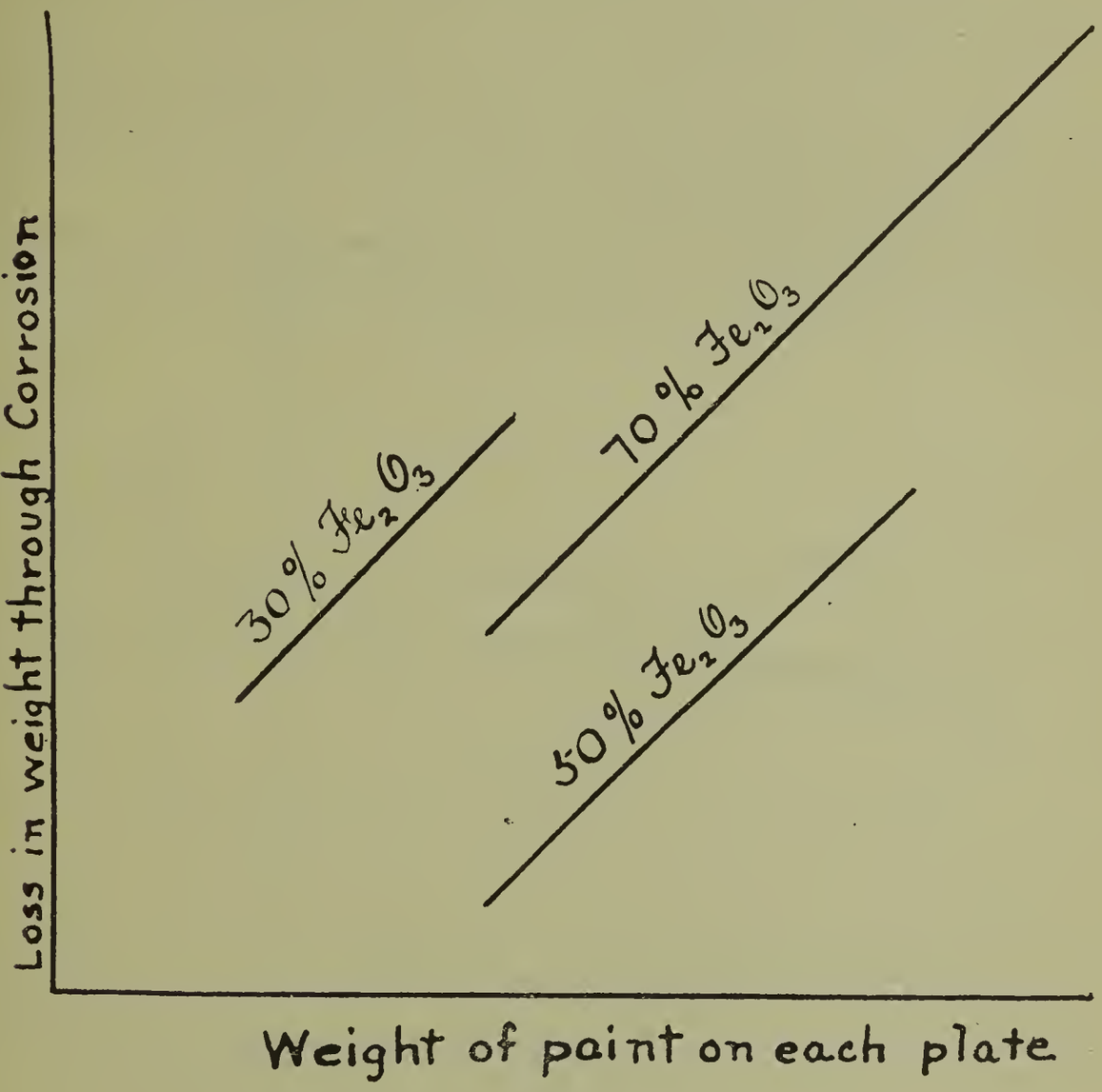


FIG. 6.

proportional to the rate of movement, even at velocities of from 30 to 40 miles per hour (1,300-1,800 cm./sec.). Clearly the two phenomena are entirely different.

## A NEW THEORY OF THE CORROSION OF IRON

As none of the recognized theories of corrosion is able to account for the foregoing anomalies, it is evident that a new and more comprehensive theory is required. In a recent communi-

cation to the Chemical Society the author has proposed one such,[15] according to which:

1. Iron, in coming into contact with liquid water in the presence of air or oxygen[16] s l o w l y oxidizes to ferrous hydroxide. This, however, is produced in the colloidal condition—a state in which it is usual for many substances to be particularly reactive chemically.

2. This ferrous hydroxide hydrosol now undergoes oxidation to a higher hydroxide hydrosol, ferric hydroxide sol being produced in the most favorable circumstances.

3. This higher hydrosol is now alternately reduced in contact with the iron and oxidized again by atmospheric oxygen, thus catalytically accelerating the oxidation of the metal.

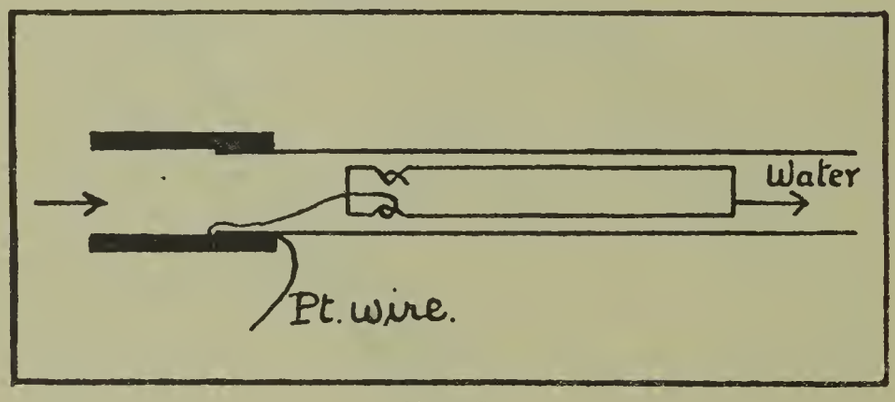


FIG. 7.

4. When the sol flocculates or precipitates out, it yields rust.

According to this theory, therefore, the corrosion of iron is at first a very slow process, but is rapidly accelerated by the catalytic activities of oxidation products of iron in colloidal form.

This auto-colloid catalytic theory enables an explanation to be given for the curious results obtained in moving water. Gentle movement serves to bring up fresh supplies of oxygen and hence to accelerate corrosion. As the rate of flow is increased, however, the catalytic hydrosols tend to be washed away, and with high velocities are completely washed away as rapidly as formed, and

[15] Friend, J. Chem. Soc., 1921, **119**, 932.

[16] The vexed question, of purely academic interest, as to whether or not absolutely pure iron will rust in the presence of absolutely pure water and oxygen is not here a matter of concern. The substances are assumed to be of average purity only, and all authorities agree that under such conditions rusting readily takes place.

are thus unable to act catalytically upon the metal, which in consequence only oxidizes with extreme slowness. In the absence of these colloids, therefore, iron is relatively "noble" or inert towards aerated waters.

The colloidal hydroxides may, however, be removed or destroyed by other than mechanical means, and if this theory is correct it will be clear that all processes, whether physical or

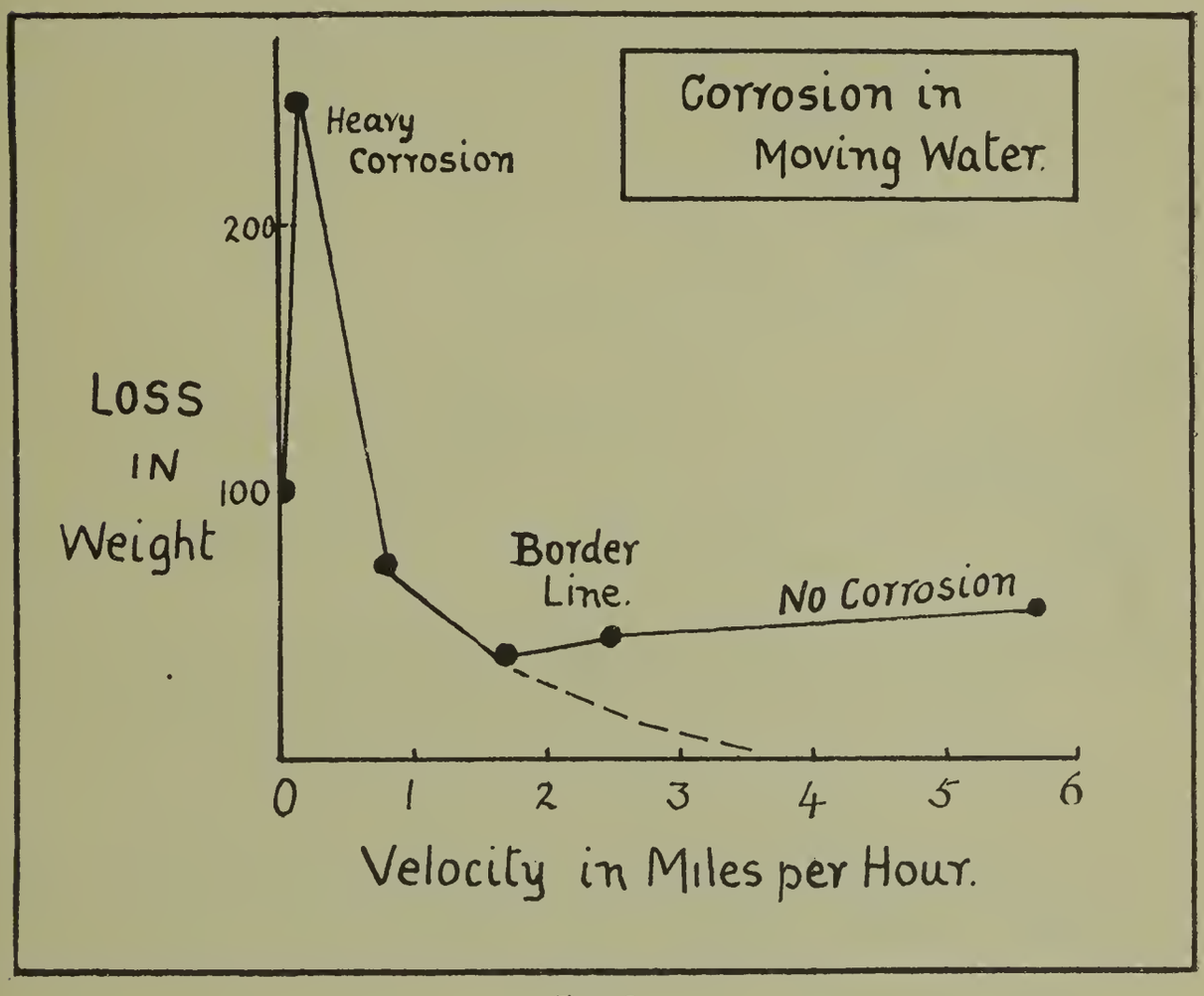


FIG. 8.

chemical, which effect the precipitation of positive colloids should tend to retard corrosion; and, on the other hand, those which tend towards the stabilization of positive colloids will enhance corrosion.

It is neither necessary nor desirable to detail the whole of the evidence in favor of this theory, but one or two of the more interesting results may be briefly referred to.

*A.* It is well known that positive colloids are readily precipi-

tated by anions, and the order of precipitation of ferric hydroxide sol by various anions is as follows[17]:

Chlorides and nitrates,
Sulphates,
Chromates,

the chlorides and nitrates being least active and chromates most active.

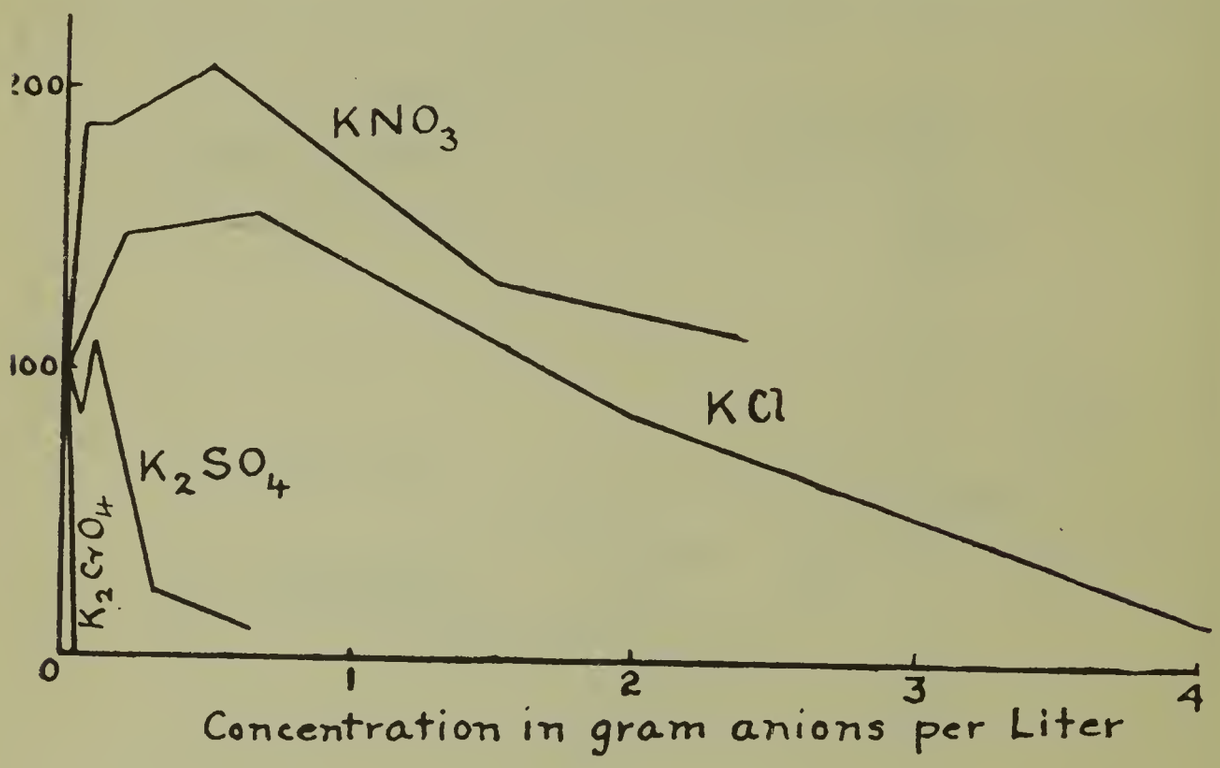


FIG. 9.

It is to be anticipated, therefore, that if the colloidal theory of corrosion is correct, addition of inorganic salts to water will tend—

1. To increase the corrosive action on iron by enhancing its solvent properties on the metal.

2. As the concentration of the salt increases, to reduce the corrosion, not merely by reducing the amount of dissolved oxygen, but also by precipitating out the ferric hydroxide sol and thus tending to remove the catalyst as rapidly as it forms.

3. Higher concentrations of chlorides will be required than of sulphates and chromates to inhibit corrosion. Now this is exactly

[17] See the results of Hardy, Zeitsch. physikal. Chem., 1900, **37**, 385. Freundlich, ibid., 1903, **44**, 144. Linder and Picton, J. Chem. Soc., 1905, **87**, 1992.

what is found to be the case, as is evident from the data[18] in Table I, shown graphically in Fig. 9, in which are given the effects of potassium salts of the above-mentioned acids at room temperatures. The concentrations of the salts are expressed along the abscissa in gram molecules (that is, gram anions) per litre, and the corrosive actions expressed relatively to water, which is taken as 100.

TABLE I.

| Gram anions of $KNO_3$ per litre | Relative Corrosion at 13.5° C. | Gram anions of KCl per litre | Relative Corrosion at 15° C. | Gram anions of $K_2SO_4$ per litre | Relative Corrosion at 15° C. |
|---|---|---|---|---|---|
| 0. | 100 | 0. | 100 | 0. | 100 |
| 0.15 | 183 | 0.2 | 149 | 0.03 | 70 |
| 0.50 | 210 | 0.67 | 155 | 0.06 | 115 |
| 1.50 | 133 | 2.0 | 88 | 0.09 | 120 |
| 2.40 | 114 | 4.0 | 16 | 0.29 | 23 |
| | | | | 0.58 | 14 |

Since relatively high concentrations of chlorides are required to precipitate ferric hydroxide sol, it will now be evident why, as indicated in Fig. 3, the corrosion and solubility curves for sodium chloride manifest a general similarity, whereas in the case of the sulphates, which are more powerful precipitants, the fall in the corrosion curve is much greater than the reduced solubility of the oxygen would lead us to expect (Fig. 2).

Alcohol, on the other hand, is not an electrolyte, but it tends to precipitate ferric hydroxide sol by dehydration and thus to reduce corrosion. It will be observed (Fig. 5) that most of the corrosion has been inhibited when sufficient alcohol has been added to yield the hydrate $C_2H_6O.3H_2O$— which supports the theory.

*B.* The colloid theory enables us to explain the curious effect of rise of temperature upon the relative corrosivities of distilled water and sea water. Ferric hydroxide sol is very stable and the liquid may be boiled under favorable conditions without precipitation. But the addition of small quantities of electrolytes readily causes its precipitation upon rise of temperature. In the case of sea water, therefore, the normal tendency to increased

[18] Calculated from the results given by Friend and Barnet, *loc. cit.* Very small quantities of potassium chromate inhibit corrosion.

corrosion with rise of temperature is in part counteracted by the inhibiting action due to the increased precipitation of the catalytic sol, with the result that, relatively to distilled water at similar temperatures, the rate of corrosion falls.

*C.* It is well known that protective colloids, while tending to prevent the precipitation of inorganic sols, also reduce the catalytic activity of the latter. Thus the addition of small quantities (of the order of 0.01 percent) of starch, gelatin, etc., to colloidal platinum reduces its power of catalytically decomposing hydrogen peroxide. The present writer has found that similar results are obtained in connection with the corrosion of iron, small quantities of organic colloids greatly reducing the corrosion of the metal both in neutral[19] and in acid[20] solution. Experiments carried out with 0.2 percent solutions of sucrose, gum acacia, potato starch, dextrin, gelatin, egg albumin, and agar in neutral solution indicate that this is the order in which they inhibit corrosion, the agar being most powerful and the sucrose the least. This order, it is interesting to note, is substantially the same as that found by Iredale[21] to hold in the reduction of the catalytic activity of colloidal platinum towards hydrogen peroxide.

The influence of colloids upon the solution of iron in dilute acids is particularly striking, the following results being typical:

| Concentration of $H_2SO_4$ | Gum Acacia percent | Mean Losses in Weight of Iron | Relative Corrosions |
|---|---|---|---|
| Normal | 0.0 | 0.0775 | 100 |
| | 0.2 | 0.0254 | 33 |
| | 0.5 | 0.0212 | 27 |
| 1/5 Normal | 0.0 | 0.0624 | 100 |
| | 0.2 | 0.0165 | 26 |
| | 0.5 | 0.0115 | 18 |

The foregoing data are of interest as bearing upon the anomalous results, to which reference has already been made, obtained with painted iron plates continuously immersed in water. The paint is essentially colloidal in structure and the linoxyn or oxidized coat of linseed oil functions as a protective colloid, and

[19] Friend, J. Chem. Soc., 1921, **119**, 932.
[20] Unpublished results by Mr. J. H. Dennett and the Author.
[21] Iredale, J. Chem. Soc., 1921, **119**, 109.

thus retards the catalytic activity of the ferric hydroxide sol, reducing the rate of corrosion. A very thin film of the oil, however, suffices to do that, and further thicknesses merely increase the quantity of protected colloidal hydrosol and thus by pure mass action increase the rate of corrosion. The anomalous behavior of the paint thus receives a ready explanation.

*D.* Finally, it may be mentioned that the influence of radioactive substances upon the rate of corrosion is in entire harmony with the author's colloid theory. Radium emanations are known to effect gradually the precipitation of ferric hydroxide sol[22] and the author has shown that under the influence of radium rays iron corrodes considerably less rapidly than otherwise.

## CONCLUSION.

It is shown that none of the recognized theories of corrosion will explain all the observed phenomena, and an account is given of a new theory which has recently been put forward by the author to explain the anomalies.

*Municipal Technical School,*
*Birmingham, England,*
*May 23, 1921.*

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## DISCUSSION.

W. E. HUGHES[1] (*Communicated*): The mass of publications good, bad, and indifferent, that have been made upon the subject of the corrosion of iron tends to obscure the most important truth that we know, even today, very little about the root cause or causes of corrosion. Dr. Friend has done good service to science by (impliedly) drawing attention to that fact, both in the present and in other recently published papers. The anomalies cited by him cannot, it is certain, be easily, if at all, harmonized with any existing theory, and Dr. Friend is to be congratulated upon, first, being bold enough to propose

[22] Fernau and Pauli, Biochem. Zeitsch., 1915, **70**, 426. Jorissen and Woudstra, Chem. Weekblad, 1912, **9**, 340.

[1] Electrometallurgist, London.

a new and more comprehensive theory, supported by newly found facts, and, secondly, upon presenting his views to a meeting of the American Electrochemical Society, where they are likely to obtain much more serious attention and discussion than their presentation elsewhere has received.

Already, Dr. Friend's view seems to have received a certain measure of confirmation from the observations of another investigator. He points out that the first product of the interaction of iron and liquid water in presence of air or oxygen is colloidal ferrous hydroxide, and the next product is ferric hydroxide hydrosol. It is most interesting and opportune that A. Ackermann should have quite recently published his observations on "The Microscopic Forms of Rust."[2] He states that the forms exhibited by rust (as viewed under the microscope) depend in the first place on the formation of ferric hydroxide, and that this "colloidal substance" assumes forms and passes through formation processes which are very like the forms and processes which occur in organized nature. Thus, both Friend and Ackermann are agreed that a colloidal substance is the first product of a series of reactions which finally result in rust.

While establishment of the fact of the formation of a colloidal substance will help one to understand certain anomalous facts concerning corrosion, yet one is not really much nearer a comprehension of the fundamental cause. What forces operate to produce the colloid? Is there a detachment of iron atoms from the surface of the metal under the operation of some force usually camouflaged under the name "solution pressure;" or do the corrosive agents attack the iron atoms *in situ*? In either case, what are the forces that operate to cause the conjunction of the iron atoms and hydroxyl groups of which ferrous and ferric hydrosols are composed? It is suggested that in the answers to these questions lies the statement of the cause of the corrosion of iron, and that before these answers can be given, our knowledge of atomic and intra-atomic forces must have become much greater than it is today. Yet, notwithstanding that Dr. Friend's paper seems to

[2] Koll. Zeits., 1921, 28, 270.

leave the fundamental problem untouched, he has undoubtedly led us a step nearer to it, and he certainly offers us a reasoned and reasonable explanation of certain facts which hitherto have seemed without any well-defined and intelligible explanation at all.

F. N. SPELLER[3] (*Communicated*): While Dr. Friend's new theory of corrosion offers an interesting explanation of some of the apparent inconsistencies of the electrolytic theory, it should really be regarded as an extension of, not a substitute for, the latter theory. The fundamental reaction,

$$Fe + 2H^{+} \rightarrow Fe^{++} + H_2$$

is too well established to be replaced by any but the most extensive and revolutionary set of experiments. It has been shown, for example, that most natural or treated waters (excluding those which are distinctly on the acid side) will not corrode appreciably in the absence of free dissolved oxygen, which tends to combine with and remove the polarizing film of hydrogen and allow the reaction to proceed. Every one of Dr. Friend's very interesting series of experiments can be explained equally well on the entirely reasonable hypothesis, consistent with the electrolytic theory, that colloidal ferric hydroxide catalyzes this secondary depolarizing reaction between the hydrogen film and the dissolved oxygen.

Without attempting to minimize the value or suggestiveness of Dr. Friend's hypothesis, in connection with engineering experiments, certain facts have been learned which are not, at first sight at least, entirely consistent with Dr. Friend's theory, and it may be well to mention these at this point.

In operating the iron deactivator for the removal of dissolved oxygen[4] considerable colloidal ferric hydrate is formed. In order to flocculate this colloid iron for clear filtration about 10 to 25 p.p.m. of alkalinity is necessary, but this amount of alkalinity has been found to have practically no influence on the rate of oxygen removal. Furthermore, in some tests recently made on corrosion of boiler water at temperatures of 65° and 165° C. with various alkalinities up to 250 p.p.m. only a relatively small difference in corrosion was found as measured by the amount of oxygen re-

[3] Metallurgical Engineer, National Tube Co., Pittsburgh, Pa.

[4] Described in paper on "Practical Means of Preventing Corrosion of Iron and Steel where not Exposed Directly to the Atmosphere" by F. N. Speller, Am. Electrochem. Soc., 1921, **39**, 141.

moved, so that in hot water the amount of colloids present appears to have little, if any, influence on the rate of corrosion. Incidentally, we have found that deactivators maintain their rate of corrosion to a remarkable degree after the iron sheets become thickly coated with flocculent rust, which one might expect would act as a protective coating and slow down the reaction. While these deactivators have been operated for three or four years with intermittent flow, a period of rest up to 36 hours does not seem to accelerate the reaction, as Kestner claims.[5]

We cannot agree that the difference in corrosion of iron in hot and cold water is relatively less than with distilled water, so that this would not support Dr. Friend's theory. Our tests indicate on the whole considerably more corrosion in hot salt water compared with hot fresh water. Furthermore, it is generally known that pipes carrying hot salt water in Atlantic City hotels fail in a much shorter time than pipes carrying fresh water at about the same temperature.

Dr. Friend's theory explains some anomalies of corrosion in cold water and may be of aid in forming a more comprehensive theory of corrosion, but in the writer's opinion the electrolytic theory with all its shortcomings has proved too useful to be discarded at this time.

J. Newton Friend (*Communicated*): The author's sincerest thanks are due for the very kind reception accorded to his paper. He only regrets that the distance prevented his reading the paper in person, as many suggestive points might have been dealt with to mutual advantage. When discussing his theory at the Chemcial Society (London) the author stated[6] that the ionic theory was not "in itself sufficient to account for all the phenomena attendant upon the corrosion of iron." This sums up the author's attitude; not necessarily to d i s c a r d earlier theories, but to s u p p l e m e n t them. To this extent the author agrees with the remarks of Mr. Speller. It would appear that in ordinary cases of corrosion, two types of reaction proceed simultaneously.

1. *Solution*—An ionic reaction, rendered possible by the presence of dissolved salts and accentuated when the metal is complex, as in the case of cast iron, by differences of potential between the ferrite and the other constituents.

[5] "Degassing and Purification of Boiler Feed Water" by Paul Kestner of Paris. Presented before the Institution of Mechanical Engineers in London, March 4, 1921.
[6] J. Chem. Soc., 1921, **119**, 932.

2. *Catalysis*—The catalyst being colloidal iron hydroxide, the corrosion of pure electrolytic iron in distilled water proceeds mainly by reaction II. In the presence of certain salts, reactions I and II may both be important. Acid attack comprises reaction I, probably exclusively, for Spring[7] has shown that while iron salts in neutral solution invariably give a pronounced Tyndall effect, indicative of the presence of a colloid, the effect disappears entirely on addition of acid. Looked at from this point of view, it will be seen that corrosion is really the algebraic sum of two effects, and many apparently contradictory results admit of explanation if this is recognized. Thus, for example, take the influence of temperature, to which Mr. Speller refers. Rise of temperature, coupled with the presence of dissolved salts, tends to coagulate iron hydroxide sol, so that the corrosion due to reaction II is reduced. But rise of temperature accelerates the rate of solution, of the metal, *i. e.*, reaction I, and the final result must therefore depend upon the relative magnitudes of the alterations in reactions II and I.

Mr. Speller cannot agree that the difference in corrosion of iron in hot and cold seawater is relatively less than with distilled water. That depends partly upon what is meant by "hot." The present author has specified the temperature. He finds, as the mean result of numerous experiments, that at about 5° C. 3 percent salt water is about 50 percent more corrosive than distilled water; whilst at room temperature there is little to choose between the two. Analogous results have been obtained with seawater, whilst at 30° C. seawater was found to be slightly but decidedly less corrosive than distilled water. The author's experiments were carried out with pure electrolytic iron foil, both liquid and metal being at rest. So that reaction I was reduced to a minimum. With commercial metal, particularly cast iron, there are so many points of irregularity, whether chemical or physical, that electrolytic action is readily set up, reaction I being thereby favored. Hence it may well be that the sum total of the corrosion in these cases is increased, in accordance with Mr. Speller's experience.[8] Clearly the two cases are not strictly com-

[7] Bull. Acad. Roy. Belg., 1899, (iii) 37, 174.

[8] So far as the present author is aware no quantitative experiments have been carried out along these lines with commercial varieties of iron and steel. The difficulty lies in obtaining reliable "repeat" results when the experiments are carried out at temperatures appreciably above atmospheric partly on account of the disturbing effects of evaporation.

parable. The reason for using pure iron foil is that it enables the different factors to be tracked down one by one in a manner that is not possible with commercial forms of the metal.

Finally the author would like, if permitted, to express his deep regret at the sad loss sustained by the Society in the death of Professor Jos. W. Richards. The author met Professor Richards in London shortly after this paper had been forwarded to the Society and has felt the loss to be a distinctly personal one.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# RUST PREVENTION BY SLUSHING.[1]

By Haakon Styri[2].

It is of great importance to many manufacturers to have a method of preventing rust on steel parts, which cannot be given a permanent coating of paint or metal.

Tools, arms, ball-bearings are among the products which must be protected with a temporary covering, such as grease. It happens, however, as we have found on slushed balls and bearings in our stock rooms that rust develops under the slushing grease, and it happens also that material in process will rust.

In order to eliminate these difficulties we have undertaken a rather thorough investigation, and the results we have found may be of interest.

The rust found on material in stock must have developed after slushing, because all material is very thoroughly inspected immediately before slushing.

It was, therefore, natural first to investigate whether different slushing greases would give different results. But the experiments made on six different greases, some of which contained bichromate, gave no indication as to which was the best. We found traces of rust under all of them after several months' exposure to the atmosphere in the factory. Cleaning in kerosene or gasoline before slushing gave no different result, but cleaning in alcohol always produced more rust. A variation of temperature of the slushing greases gave no information. We found, however, that rust generally formed where the parts were most readily touched in handling and found sometimes distinct finger-prints of rust. This was, of course, a clear indication that perspiration was one cause of rust. In proof some parts were

[1] Manuscript received August 13, 1921.

[2] Chief S. K. F. Research Laboratory, Philadelphia, Pa.

slushed immediately after polishing with no handling, and no rust developed in the testing method then used.

It was expected that presence of moisture would cause rust, and several experiments were made to determine at what point introduction of moisture was of importance. When parts were taken directly from polishing and sprayed with water corroded spots showed up shortly after slushing in hot grease. But if the parts after spraying had been cleaned in kerosene and blown dry with compressed air before slushing, little rust was developed. Some rings were polished and boiled in distilled water, and dried by their own heat before they were slushed in hot grease. Several corroded spots were found, but it was noticed that a slight film was left after drying, so a slight amount of salt must have been dissolved in the water. Presence of moisture in the slushing grease was proven to produce corroded spots on the rings when they were slushed hot. Some rings were dipped in soda solutions of different concentrations and dried by their own heat before slushing, and it was found that those dipped in the strongest solutions gave the best results, although not perfect. It was also found that when rings were dipped in hot soda or similar solution and dried and later exposed to humid atmosphere without slushing they would rust rapidly.

The method so far used for cleaning had not satisfactorily removed the soluble salt from the surface of the steel, and the trace left, together with moisture, caused rust, even when the surface was well slushed. The solutions we had used for finish grinding of material in process, namely, soda or similar alkaline products, did not protect the parts from rusting in humid atmosphere, even when exposed for only short time, so our problem was therefore to find a better method of cleaning before slushing as well as to find a method of protecting parts in process. It was necessary also to have such experimental conditions that we did not need to wait a long time for results in our experiments. Our record of humidity of atmosphere had shown us that at a relative humidity above 60 percent rust started to form and interfere with production.

The Bureau of Mines in Pittsburgh had recently conducted experiments on rusting of gun barrels in humidors with interest-

ing results. We adopted, therefore, a humidor for our exposure tests with the greatest advantage, as we got results in a week to fourteen days when we previously had waited many months.

We realized that if we could protect material in process we had in fact obtained a method for cleaning before slushing. Our preliminary experiments had shown that it was necessary to use an aqueous washing liquid for the elimination of salts on the surface and also that it was important to have an immediate protection against action of the atmosphere. Consequently washing in an emulsion of soap and mineral oil was experimented with, where the aqueous solution should dissolve any salt and emulsify fats and fatty acids on the surface of the steel and the oil particles would form a protective coating when they adhered to the surface.

For comparative tests specimens were first dipped in a 5 percent salt solution and then washed respectively in soap emulsion, soda solution or gasoline before they were slushed in different compounds. The results showed clearly that washing in aqueous solution was better than washing in gasoline, but no difference could be found due to greases from five different manufacturers.

Repeating such test with highly polished balls which had been cleaned in gasoline and dried, gave somewhat erratic results, indicating that slight variation in test conditions such as variation in concentration and time of washing may be of great importance. The following experiments were made to investigate this.

Balls as received from stock were cleaned in kerosene and carefully examined for freedom from rust. They were then dipped for two minutes in solutions made up of equal parts MgCl, NaCl and KCl in total concentration 0.1, 0.5 and 1 percent. Thereafter they were for comparison washed in various cleaning solutions at room temperature and placed in humidor for one hour. Then they were again dipped in the solution for two minutes, washed and placed in humidor. This was repeated seven times, whereafter the balls were left in humidor over night and examined in the morning. Dippings and washings were repeated next day, and after a second night in humidor the balls were again examined. Results are shown in Table I. The experiment was repeated with boiling washing solutions with the results

## TABLE I.

Balls ¾ inch cleaned and inspected. Dipped at room temperature into a salt solution of equal parts of magnesium, sodium and potassium chlorides, then into cleaning solution at room temperature. Repeated dipping in salt solution and cleaning solution at hour intervals. Inspected after 24 hours, again after 48 hours. Balls placed in humidor after each dipping process. Balls run in duplicate, designated as "A" and "B".

| Cleaning Solution | Percent Oil | RESULTS AFTER 24 HOURS | | |
|---|---|---|---|---|
| | | 0.1 Percent Salt Sol. | 0.5 Percent Salt Sol. | 1.0 Percent Salt Sol. |
| Alkaline phosphate 3 percent solution ..... (a) | .. | Slight tarnish on both | A and B Many tarnished spots | A One corroded spot and slight tarn. B Slight tarn. |
| Same..... | 10 | A Many small rust spots B Slightly tarnished | A and B Many rust spots | A and B Many rust spots |
| Soda solution 4 percent sodium carbonate ..... | .. | A and B Slightly tarnished | A and B Slight tarnish | A and B Very small corroded spots |
| 8 percent soda solution..... | .. | A and B Slightly tarnished | A and B O. K. | A and B Few very small spots |
| Alkaline phosphate 3 percent solution ..... (b) | .. | A and B Slightly tarnished | A and B Slight tarnish | A and B Many tarnished spots |
| Same..... | 10 | A and B Slightly tarnished | A and B Slight tarnish | A and B Many tarnished spots |
| 2 percent sodium oleate soap solution ..... | .. | A and B Slight tarnish | A and B Few tarnished spots | A Few spots. B Many spots and ring at contact pt. |
| Same..... | 10 | A and B Slight tarnish | A O. K. B Few tarnished spots | A O. K. B One spot |
| Same..... | 50 | A and B Slight tarnish | A and B O. K. | A and B O. K. |
| Alkaline phosphate 3 percent solution ..... (c) | .. | A and B Many small rust spots | A and B Many small rust spots | A and B Many small rust spots |
| Alkaline phosphate 3 percent solution ..... (d) | .. | A and B Many small rust spots | A and B Many small rust spots | A and B Many small rust spots |

TABLE I—*Continued.*

| Cleaning Solution | Percent Oil | RESULTS AFTER 48 HOURS | | |
|---|---|---|---|---|
| | | 0.1 Percent Salt Sol. | 0.5 Percent Salt Sol. | 1.0 Percent Salt Sol. |
| Alkaline phosphate 3 percent solution ..... (a) | .. | A Many small and one large spot. B Tarnished and a few small spots. | A and B Heavily tarnished and a few small rust spots | A Tarnished; one large spot. B Tarnished; few small spots |
| Same..... | 10 | A Many small spots<br>B Few small spots | A and B Very many heavy rust spots | A and B Very badly rusted |
| Soda solution 4 percent sodium carbonate ..... | .. | A and B Few small rust spots | A and B very many small rust spots | A Tarnished and a few spots. B Slight tarnish |
| 8 percent soda solution.... | .. | A O. K.<br>B Small spots | A and B Many corroded spots | A and B Many corroded marks |
| Alkaline phosphate 3 percent solution ..... (b) | .. | A One small spot; also slight tarn. B Slight tarn. | A and B Heavily tarnished | A and B Heavily tarn. rings at contact points |
| Same..... | 10 | A and B Slight tarnish | A Tarnished and a few small spots. B Tarnished and many spots | A and B Slight tarn. and a few small spots |
| 2 percent sodium oleate soap solution ..... | .. | A and B Couple of corroded spots | A and B Couple of small rust spots | A and B Slight tarn. corroded circles at contact pts. |
| Same..... | 10 | A O. K.<br>B Few tarnished stains | A and B Couple of small rust spots | A and B Slight tarn. and a few spots |
| Same..... | 50 | A and B Two rust spots | A and B Slight tarnish | A and B Slight tarnish |
| Alkaline phosphate 3 percent solution ..... (c) | .. | A and B Many small rust spots | A and B Many small rust spots | A and B Many small rust spots |
| Alkaline phosphate 3 percent solution ..... (d) | .. | A and B Very many rust spots | A and B Very many rust spots | A and B Very many small rust spots. |

Phosphates a, b, c and d are from different manufacturers.

TABLE II.

*Experiment Repeated Washing in Boiling Solution.*

| Cleaning Solution | Percent Oil | RESULTS AFTER 24 HOURS | | |
|---|---|---|---|---|
| | | 0.1 Percent Salt Sol. | 0.5 Percent Salt Sol. | 1.0 Percent Salt Sol. |
| Alkaline phosphate 3 percent solution ..... (a) | .. | A O. K.<br>B Few small rust spots | A and B Very small spots | A and B Slight tarnish at contact points |
| Same..... | 10 | A and B Couple of small rust spots | A and B Couple small spots | A and B Few slight tarnish stains |
| Soda solution 4 percent carbonate ..... | .. | A and B Couple of small rust spots | A and B Corroded rings at contact points and a few small spots | A and B Slight tarnish |
| 8 percent soda solution..... | .. | A and B Couple of small rust spots | A and B Slight tarnish at contact points | A and B Couple rust spots and slight tarnish |
| Alkaline phosphate 3 percent solution ..... (b) | .. | A and B Couple of small rust spots | A and B Couple small rust spots | A and B Slight tarnish |
| Same..... | 10 | A and B Two small rust spots. | A Few small spots<br>B Heavily tarnished stains at contact point | A and B Couple small rust spots |
| 2 percent sodium oleate soap solution ..... | .. | A and B O. K. | A and B O. K. | A and B O. K. |
| Same..... | 10 | A and B O. K. | A One rust spot<br>B O. K. | A Slight tarnish<br>B O. K. |
| Same..... | 50 | A and B O. K. | A and B O. K. | A and B O. K. |
| Alkaline phosphate 3 percent solution ..... (c) | .. | A and B Very many small rust spots | A and B Couple rust spot stains at contact points | A Small rust spots; tarn. at contact points<br>B Small rust spots |
| Alkaline phosphate 3 percent solution .....(d) | .. | A and B Couple small rust spots | A and B Many small rust spots | A and B Couple rust spots |

TABLE II—*Continued*

| Cleaning Solution | Percent Oil | RESULTS AFTER 48 HOURS | | |
|---|---|---|---|---|
| | | 0.1 Percent Salt Sol. | 0.5 Percent Salt Sol. | 1.0 Percent Salt Sol. |
| Alkaline phosphate 3 percent solution ..... (a) | .. | A Couple of small spots B Many small spots | A and B Slightly tarnished | A and B Very badly tarnished |
| Same..... | 10 | A and B Few small spots | A and B A few small spots and slightly tarnished | A and B Heavily stained B Few small spots |
| Soda solution 4 per cent. sodium carbonate ..... | .. | A and B Few small spots | A and B Tarnished rings at contact points | A and B Few small spots |
| 8 percent soda solution.... | .. | A and B Few small spots | A and B Tarnished rings at contact points | A and B Few small spots |
| Alkaline phosphate 3 percent solution .....(b) | .. | A and B Few small spots | A and B Few small spots and tarnished rings at conact points | A and B Few slight stains |
| Same..... | 10 | A and B Few very small spots | A and B many small spot A Tarnished rings at contact points | A and B Few small spots |
| 2 percent sodium oleate soap solution ..... | .. | A Two very small spots. B Heavy cor. at con. pt. | A and B O. K. | A and B Two small spots |
| Same..... | 10 | A and B O. K. | A 1 small spot. B O. K. | A and B O. K. |
| Same..... | 50 | A and B Few very small spots | A O. K. B One small circular stain at contact pt. | A and B Couple very small spots |
| Alkaline phosphate 3 percent solution .....(c) | .. | A and B Very many spots at contact points | A and B Many small spots; stains at contact point | A and B Many small spots; tarnished rings at contact points |
| Alkaline phosphate 3 percent solution ..... (d) | .. | A and B Few very small spots | A and B Very badly tarnished at contact points | A and B Few small spots, tarnish at contact points |

Phosphates a, b, c and d are from different manufacturers.

## Table III.

### *Corrosion from Perspiration*

¾-inch balls cleaned in kerosene and inspected. Dipped for 2 minutes in 1 percent salt solution (sodium chloride, potassium chloride and magnesium chloride) and 1 percent urine. Washed immediately for 5 minutes in hot washing solution. Repeated every hour as in Table I.

| Washing Solution | Material Added | Results after 24 hours | Results after 48 hours |
|---|---|---|---|
| Alkaline Phosphate 3 percent solution...(b) | | A&B. Many large tarnished spots. Circular ring at contact point. | A&B. Many large tarnished spots; ring at contact. |
| Same ..... | 20 percent Oil | A&B. Couple of heavy spots. | A&B. Many corroded spots and some tarnish. |
| 2 Percent Sod. Oleate slightly Alkaline ..... | | O.K.<br>O.K. | O.K.<br>O.K. |
| Same ..... | 20 percent Oil | O.K.<br>O.K. | O.K.<br>O.K. |
| Same ..... | 20 percent Oil<br>2 percent Sod. Carbonate | O.K.<br>O.K. | O.K.<br>One spot |
| Same ..... | 20 percent Oil<br>2 percent Phosphate (a) | A&B. Couple of spots. | A&B. Few spots. |
| Alkaline Phosphate 0.4 Excess Alkali (d) | | O.K.<br>O.K. | O.K.<br>O.K. |
| Same ..... | 20 percent Oil | A. O.K.<br>B. Couple spots at contact. | O.K.<br>Two spots at contact |
| Same ..... | 20 percent Oil<br>2 percent Sod. Carbonate | O.K.<br>O.K. | O.K.<br>O.K. |
| Same ..... | 20 percent Oil<br>2 percent Phosphate (d) | A&B. Heavy coat of tarnish. | Few spots and a heavy coat of tarnish |

given in Table II. Evidently this improves conditions. Of the washing solutions used the soap emulsion is the best.

Knowing that perspiration is one source of rust producer and wanting to get the experiments as close to practical conditions as possible similar experiments were repeated with a 1 percent

## Table IV.

### *Continuous Stirring of Washing Liquid.*

Washing solution was stirred continuously while the balls were being washed. ¾-inch balls were used after being cleaned and inspected. The balls were first dipped in a 1 percent solution of magnesium chloride, potassium chloride and sodium chloride and 1 percent urine for two minutes, then washed immediately in a washing solution for five minutes. Repeated dipping and washing every hour. Balls placed in humidor after washing and over night. Inspected after 24 hours and after 48 hours.

| Washing Solution | Material Added | Results after 24 hours | Results after 48 hours |
|---|---|---|---|
| Alkaline Phosphate 3 percent solution...(a) | 20 percent Oil | A&B. Many large spots. | A&B. Many large corroded spots. |
| Sodium Oleate, 2 percent solution ..... | 20 percent Oil | A&B. O.K. | A&B. O.K. |
| Same ..... | 20 percent Oil 2 percent Soda | A&B. Few small corroded spots. | A&B. Few Corroded spots |
| Same ..... | 20 percent Oil 2 percent Phosphate (a) | A&B. Heavy coat of tarnish. | A&B. Very many corroded spots |
| Alkaline Phosphate, 3 percent solution ...(d) | 20 percent Oil | A&B. Corroded ring at contact point. | A&B. Corroded ring at contact point. |
| Same ..... | 20 percent Oil 2 percent Soda | A&B. Corroded ring at contact point. | A&B. Corroded ring at contact point. |
| Same ..... | 20 percent Oil 2 percent Phosphate (d) | A&B. Heavy coat of tarnish. | A&B. Heavy coat of tarnish. |

Phosphates a and d are from different manufacturers

solution of salt mixture to which was added 1 percent urine for the first dipping. The washing after dipping in the salt solution was continued five minutes because other experiments had shown that a too short washing gave erratic results. Table III shows the effect of good cleaning.

In practice the washing liquid would not be kept quiet, so experiments while stirring were made with the results shown in Table IV. An excess of alkali is not advantageous and the best results are again with a soap emulsion.

The Tables I-IV give only the results of washing in different

## Table V.

*Bearings Washed Five Minutes in Soap Emulsion.*
*In Humidor two weeks.*

| Grease Used | Percent Oil Added | Temp. of Slushing | Temp. of Washing 2 Percent Soap 49 Oil 49 Water | Results |
|---|---|---|---|---|
| HB Slushing Grease ..... | Nil | 200 F. | 80 F. | Few spots on inner raceway. O.K. |
| Same ..... | Nil | 200 F. | 210 F.* | Very many small spots on outside of O. D. Inner race, bore rusty. |
| Same ..... | 25 | 140 F. | 80 F. | O.K.<br>O.K. |
| Same ..... | 25 | 140 F. | 210 F.* | O.K.<br>O.K. |
| Same ..... | 50 | 115 F. | 80 F. | O.K.<br>O.K. |
| Same ..... | 50 | 115 F. | 210 F.* | O.K.<br>O.K. |
| Petroleum Jelly....(a) | Nil | 150 F. | 80 F. | Few spots on inner race. One spot on O. D. |
| Same ..... | Nil | 150 F. | 210 F.* | O.K.<br>O.K. |
| Petroleum Jelly.....(b) | Nil | 150 F. | 80 F. | O.K.<br>O.K. |
| Same ..... | Nil | 150 F. | 210 F.* | O.K.<br>O.K. |

* At 210 F. the washing solution separated in two layers, oil on top.
The a and b petroleum jellies are from different manufacturers.

solutions with a short time exposure to humid atmosphere. But it is clear that the oil film left after washing in soap emulsion gives better protection than when no film is present. When steel is to be kept a long period, it must evidently be given a better coating than such thin oil film which will gradually drain off. Experiments were run to find a good method of applying slushing greases after a washing in soap emulsion.

Most naturally it was first tried whether a slushing grease could not be applied directly on a soap emulsion, and the experi-

## Table VI.

*Washing in Soap Emulsion Made of Different Percentages of Soap, Using Light and Heavy Oil, and Removing Washing Liquid with Kerosene. In Humidor One Week.*

| No. Balls | Washing 5 min.; Stirring Room Temp. | | Extra Washing Room Temp. | Slushed in Cylinder Oil Room Temp. | Slushed in Petroleum Jelly 110 F. |
|---|---|---|---|---|---|
| | Percent Soap | Percent Light Oil | | | |
| 2 | 2 | 5 | Kerosene | Both O. K. | ..... |
| 2 | 2 | 10 | Kerosene | Both O. K. | ..... |
| 2 | 2 | 20 | Kerosene | Both O. K. | ..... |
| 2 | 2 | 5 | Kerosene | ..... | Both O. K. |
| 2 | 2 | 10 | Kerosene | ..... | Both O. K. |
| 2 | 2 | 20 | Kerosene | ..... | Both O. K. |
| 2 | 4 | 5 | Kerosene | Both O. K. | ..... |
| 2 | 4 | 10 | Kerosene | Both O. K. | ..... |
| 2 | 4 | 20 | Kerosene | 1 ball O. K. 1 ball with small rust spot | ..... |
| 2 | 4 | 5 | Kerosene | ..... | Both O. K. |
| 2 | 4 | 10 | Kerosene | ..... | Both O. K. |
| 2 | 4 | 20 | Kerosene | ..... | 1 ball O. K. 1—few small rust spots |
| | Percent Soap | Percent Heavy Oil | | | |
| 2 | 2 | 5 | Kerosene | Both slightly rusted retainer | ..... |
| 2 | 2 | 10 | Kerosene | 1 ball O. K. 1 ball rusted ret. | ..... |
| 2 | 2 | 20 | Kerosene | Both O. K. | ..... |
| 2 | 2 | 5 | Kerosene | ..... | Both O. K. |
| 2 | 2 | 10 | Kerosene | ..... | Both O. K. |
| 2 | 2 | 20 | Kerosene | ..... | Both O. K. |
| 2 | 4 | 5 | Kerosene | Both O. K. | ..... |
| 2 | 4 | 10 | Kerosene | 1 small rust spot on each | ..... |
| 2 | 4 | 20 | Kerosene | 1 ball O. K. 1 ball with small rust spot | ..... |
| 2 | 4 | 5 | Kerosene | ..... | Both O. K. |
| 2 | 4 | 10 | Kerosene | ..... | Both O. K. |
| 2 | 4 | 20 | Kerosene | ..... | Both O. K. |

ments made on spherical bearings reported in Table V show this can be done. However, there is this practical difficulty. That when a great many bearings should be washed in a soap emulsion, necessarily under stirring, some dirt will gradually collect and will be attached to the oil film on the bearing and cause a noisy

## Table VII.

*Tests on Washing in Pure Soap and Removing Washing Liquid with Hot Oil. Kept in Humidor one week.*

| No. Balls | Washing 5 Min. Stirring Room Temp. | Extra Washing 8 Min. Stirring 175 F. | No Slushing | Slushed in Cylinder Oil | | Slushed in Petroleum Jelly 110 F. |
|---|---|---|---|---|---|---|
| | | | | Room Temp. | 175 F. | |
| 2 | 2 percent soap | light oil | 1 B O. K. | ..... | ..... | |
| | | | 1 B Rusted slightly | ..... | ..... | |
| | | | | ..... | ..... | |
| 2 | 2 percent soap | light oil | ..... | 1 B O. K. | ..... | |
| | | | | 1 B Tarn. slightly | | |
| 2 | 2 percent soap | light oil | ..... | ..... | Both O. K. | |
| 2 | 2 percent soap | light oil | ..... | ..... | ..... | 1 Ball O. K. 1 Ball small rust spot |
| 2 | 4 percent soap | light oil | Both O. K. | ..... | ..... | |
| 2 | 4 percent soap | light oil | ..... | Both O. K. | ..... | |
| 2 | 4 percent soap | light oil | ..... | ..... | Both rusted | |
| 2 | 4 percent soap | light oil | ..... | ..... | ..... | 1 Ball O. K. 1 slightly rusted |

running. It was therefore necessary to apply an intermediate washing of bearings covered with oil emulsion during manufacturing in order to clean out dirt particles, and which would not again induce formation of rust before or after slushing. It was first tried to omit such intermediate washing by heating a soap emulsion to such temperature as would allow rapid demulsification and then to submerge parts into the aqueous solution without stirring at a point where the oil layer was kept away and draw them up through the oil layer another place. But on the contact surface between the oil and soap solution a fine dirt layer would be suspended and no vigorous stirring for cleaning could be allowed. With subsequent slushing the experiment gave erratic results. For the elimination of dirt, therefore, a second washing in kerosene was tried apparently with advantage as shown in Table VI.

Under certain circumstances a pure soap solution can be used for washing when the product afterwards will not be exposed to

## Table VIII.

*Tests on Washing in Pure Soap, and Removing Washing Liquid with Hot Oil. Experiments Kept in Humidor One Week After Slushing.*

| No. Balls | Washing | Drying | Extra Washing | Slushed in Cylinder Oil Room Temp. | Slushed in Petroleum Jelly 110 F. |
|---|---|---|---|---|---|
| | 150 F. 10 min. Percent Soap | | | | |
| 2 | 2 | ..... | Light oil 175 F. | Both O. K. | ..... |
| 2 | 4 | ..... | Light oil 175 F. | Both O. K. | ..... |
| 2 | 2 | ..... | Light oil 175 F. | ..... | Both O. K. |
| 2 | 4 | ..... | Light oil 175 F. | ..... | Both O. K. |
| | 200 F. 10 min. Percent Soap | | | | |
| 2 | 2 | ..... | Light oil 175 F. | Both O. K. | ..... |
| 2 | 4 | ..... | ..... | Both O. K. | ..... |
| 2 | 2 | ..... | Light oil 175 F. | ..... | Both O. K. |
| 2 | 4 | ..... | Light oil 175 F. | ..... | Both slightly rusted retainer |
| 2 | Soap emulsion R. Temp. | 200 F. | ..... | ..... | Both O. K. |
| 2 | 4 percent soda R. Temp. | 200 F. | ..... | ..... | Both badly rusted |
| 2 | 4 percent alkaline phosphate Sol. R. Temp. | 200 F. | ..... | ..... | 1 Ball O. K. 1 rusted at ret. |
| 2 | 4 percent alkaline phosphate Sol. (washed with tepid water and dried) | ..... | ..... | ..... | Both rusted |

the atmosphere for any length of time. If that is the case, a cover of oil must follow immediately. Table VII gives the result of such experiments. We see that it is better to have a hot soap solution than a cold one, and that an addition of soda, or pure soda, or similar solution is not satisfactory.

A washing in hot soap solution with subsequent drying before slushing is also good, and it was found that steel could be kept inserted in a soap solution for a considerable time without rusting, just like it can be done in soda solution. (Table VIII.)

The drying after washing in soap (Table IX) will naturally leave a fine film of soap on the steel, and this will act as a protective coating. But if such soap coating only was left on the surface, it would liquefy in humid atmosphere and run off, and

## Table IX.

*Effects of Drying After Washing Before Slushing.*

All experiments following in humidor one week after slushing.

| No. Balls ¾-in. | Washing | Drying | Not Slushed | Slushed in Cylinder Oil Room Temp. | Slushed in Petroleum Jelly 110 F. |
|---|---|---|---|---|---|
| | 150 F. 10 min. Percent Soap | | | | |
| 2 | 2 | Own heat | Both rusted retainer | ..... | ..... |
| 2 | 2 | 150 F. | ..... | Both O. K. | ..... |
| 2 | 2 | 150 F. | ..... | ..... | Both O. K. |
| 2 | 4 | Own heat | Both O. K. | ..... | ..... |
| 2 | 4 | 150 F. | ..... | Both O. K. | ..... |
| 2 | 4 | 150 F. | ..... | ..... | Both O. K. |
| | 200 F. 15 min. Percent Soap | | | | |
| 2 | 2 | Own heat | 1 B O. K. 1—1 small rust spot | ..... | ..... |
| 2 | 2 | 200 F. | ..... | Both O. K. | ..... |
| 2 | 2 | 200 F. | ..... | ..... | Both O. K. |
| 2 | 4 | Own heat | Both O. K. | ..... | ..... |
| 2 | 4 | 200 F. | ..... | Both O. K. | ..... |
| 2 | 4 | 200 F. | ..... | ..... | Both O. K. |
| | 150 F. 10 min. | | | | |
| 2 | Soap emulsion | Own heat | Both O. K. | ..... | ..... |
| 2 | Soap emulsion | 150 F. | ..... | 1 B O. K. 1 slightly rusted | ..... |
| 2 | Soap emulsion | 150 F. | ..... | ..... | 1 B O. K. 1 slightly rusted |

a coating of stiff soap without grease or oil would not act as a lubricant and can not therefore be used in practice for ball bearings; but probably in many other cases. Some experiments were made to investigate the amount of NaCl that could be present in the soap solution without inducing formation of rust, and it was found an amount of 0.02 percent NaCl can hardly be exceeded before rust would readily form.

The experiments described give briefly the main line of investigation in the course of which a number of side questions had to be investigated. Thus, for instance, because a mineral oil emulsion

is not so stable as one of organic oil, an emulsion of the latter sort was tested out for rust protective power and was found fairly satisfactory, although not as good as a mineral oil emulsion.

Another rather serious thing occurred. We found that rings and balls in contact with cardboard or table tops nearly invariably rusted when covered with soap emulsion, whereas other parts not in contact remained clean. This was due to salts being dissolved out by the aqueous solution. After the table tops were thoroughly washed with hot soap solution, this trouble was practically eliminated.

It was also found, what we might of course expect, that bearings fitted with bronze retainers corroded when covered with soap emulsion. This happened, however, not invariably, as certain cages with a high percentage of zinc protected the steel parts from corrosion, just as it was found that galvanized iron on table tops prevented rusting. Sodium soap was less active than ammonium soap.

As to the relative weight of different slushing media for protection against rust in humid atmosphere, we do not have sufficiently extensive tests to pass final judgment. But all the tests we have made show no preference of one against another, varying from heavy mineral grease with rust inhibitors to pure mineral greases, cylinder oil and even crude oil. They are all good when free from acid and when they stick to the steel surface after a thorough cleaning of the sample. Even a soap grease is satisfactory when galvanic action will not start as when bronze cages are used. For ball bearings we have to consider that the slushing grease also ought to act as a lubricant, so that no cleaning by the customer should be necessary before assembling. We have adopted, therefore, a soft slushing grease for our product, a pure mineral jelly without adulterants.

Among other experiences we had these can be mentioned. Some of the first soap emulsions made up with ammonium oleate became slightly acid from inaccurate mixing and got a very foul smell and started rust. Later on a neutral sodium oleate has been used for grinding. With the alkaline grinding solutions previously used, it was found that, when traces of them were left on the bearings and they were washed in kerosene, rust spots were pro-

duced very rapidly, in fact, in special experiments even within five minutes. When soap emulsion is used, screens with less than 60-mesh per inch and settling tanks should be provided, to keep the grinding liquid as free as possible from grinding dirt.

We have also found that bearings were protected from rust when kept in air-tight containers filled with pure mineral grease in which solid salt was mixed and when the container was exposed to humid atmosphere.

The results described above give the principal items of examinations made on nearly 1,000 samples, by our chemists, Messrs. D. D. Stark, E. H. Smith and W. C. Schneider.

### CONCLUSION.

We have shown that a prerequisite for protection against rust by greases is a thorough cleaning of the steel parts by an aqueous solution, preferably by an oil emulsion which leaves a thin oil film for short time protection. Such oil emulsion is also a very good grinding liquid. It protects from rust and gives a fine finish.

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## DISCUSSION.

C. H. PROCTOR[1]: Have you had rusting to any extent after the product is finished?

HAAKON STYRI: No, since we introduced this method about a year ago, we have not found any rust in our material, and we have not had any notice of trouble during the process.

C. H. PROCTOR: Some two or three years ago a patent was granted for a mixture of ortho-phosphoric acid and denatured alcohol, which was used to a great extent by the automobile manufacturers in covering their bodies, etc. They immersed the bodies in this mixture and let the mixture dry on the surface before they coated it with paint. I was wondering whether any one had any experience with this combination for finished steel products?

[1] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.

HAAKON STYRI: We have tried that, like we have tried a dozen other different compounds. We cannot use it. It is all right, but we cannot use it for the simple reason that it does affect the surface slightly; the phosphoric acid affects the steel and corrodes it slightly. It gives a very adherent coating, but we must have a polished surface.

C. H. PROCTOR: In other words, the phosphoric acid forms on your surface a coating of phosphate of iron?

HAAKON STYRI: Yes.

WM. BLUM[2]: This subject of protecting steel against what might be called mild rusting conditions during storage and manufacture became important during and after the war. An extended investigation of the various slushing compounds was made by the Bureau of Standards, and the results were published in Technologic Paper 176. A number of manufacturers had the erroneous conception that by adding to the oil some substance such as a chromate, which in aqueous solutions inhibits rust, they would get better results. When, however, a small amount of aqueous chromate is mixed with oil, it does not increase the rust protection, but instead causes "slipping" of the oil.

HAAKON STYRI: I have tried different compounds with chromate in them, and I did not find any improvement over petroleum jellies.

C. H. PROCTOR: During last winter I was much interested in the rusting of steel parts, and in going over the patents I spoke of I thought it might be possible to prepare an emulsion of phosphoric acid and petroleum. I did so and took some razor blades, coated them very thinly with this combination and left the razor blades out all through the winter in the snow. At the end of the season they were absolutely free from rust.

HAAKON STYRI: That is the same thing again.

C. H. PROCTOR: But it did not seem to attack the razor blades; they were as perfect as before.

HAAKON STYRI: Did you examine them with the microscope?

C. H. PROCTOR: No, but I took an ordinary glass and examined them and could not find any rust.

[2] Chemist, Bureau of Standards, Washington, D. C.

ACHESON SMITH[3]: I would like to ask Dr. Blum if those recommendations of the Bureau of Standards for keeping rifles have ever been checked up? They issued those instructions which, as I remember, provided for cleaning with an aqueous solution first and then using some of these compounds to prevent rust. That was done probably two or three years ago. Do you know whether they have checked up the effectiveness of those recommendations at all?

WM. BLUM: I do not know whether any survey of the condition of these materials in storage has ever been made or not, or whether they know where they are.

HAAKON STYRI: Does it not come from insufficient washing before slushing in grease or oil? We have found that if there is not good washing before slushing, you will get poor results. If you do not get the salts or fatty acids and fatty oils off and get the surface perfectly clean before applying the slushing, you will get more or less rusting.

J. W. RICHARDS[4]: I was given a Japanese sword by a Japanese friend, and he told me that the way they preserve their swords from corrosion is by slushing them with an oil which contains a little very finely divided lead. I came across a reference to that in an old publication of the middle ages; that the sword-makers of Europe used that same mixture. I was talking about the "ever-sharp" pencil, and a friend of mine said: "The thing that gives way is this little tip at the end; it is in that part of the pocket where it can come in contact with the perspiration." I noticed that the tip of the one I have is rusting badly, so evidently that is the weak spot of the "ever-sharp" pencil, and the rusting is caused by its contact with the perspiration of the body. I have here a knife which Mr. Haynes gave me, made of stellite, which I have carried in my vest pocket for four years, and the polish has not come off at all, so evidently that is a material which is resistant to these conditions of perspiration. If the "ever-sharp" people would make tips of stellite they would evidently not rust.

[3] Vice Pres. and General Manager, Acheson Graphite Co., Niagara Falls, N. Y.
[4] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# TRANSFORMER OIL SLUDGE.[1]

By C. J. Rodman.[2]

Abstract.

The three types of transformer oil sludge described are the asphaltic, the soap, and the carbon. Asphaltic and soap sludges are produced most readily by oxidation of poor oil, containing unsaturates, water, small resinous bodies and certain accelerators. The carbon type of sludge is produced during electrical breakdown. Highly refined oil of the saturated paraffine series, which is carefully filtered when the dielectric strength begins to lower during operation, can be successfully used for many years.

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The better refined oils used within transformers for insulating and cooling purposes are comparatively stable to chemical change. In service, these oils are not subjected to the effects of light;[3] but during peak loads may experience a temperature rise of 50° to 70° C. In the absence of certain catalysts, these higher temperatures do not appreciably accelerate sludge formation. Transformers containing well refined oil have been in operation during the past twelve to fifteen years without any serious trouble. Examination of the good oil which has been given a few filtrations during the period indicates that the oil is as good today or even better than when it was first used.

From time to time, however, serious transformer trouble has come to the author's notice. This trouble may be largely attributed to poor oil, which gives rise to early sludging or, in drastic cases to electrical breakdown. Explosions and

[1] Manuscript received August 8, 1921.

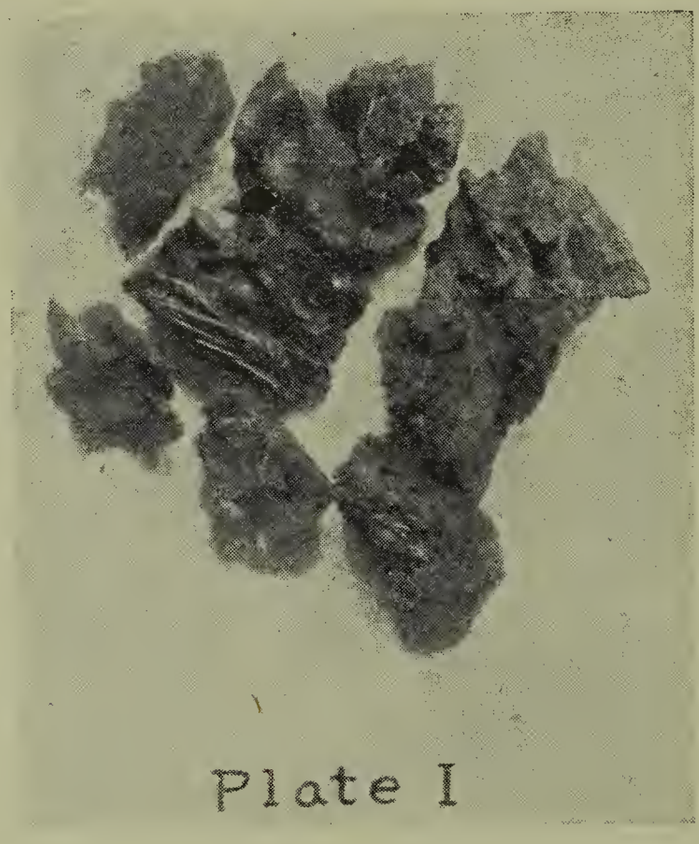
[2] Research Engineer, Westinghouse Electric and Mfg. Co., E. Pittsburgh, Pa.

[3] Bull. 7, Bur. of Stds. p. 227-234.

blowing-up of transformers are only secondary effects of electrical breakdown. With judicious selection of a good oil and its care during operation, no failure of the oil should occur within a quarter century of time.

## THE ASPHALTIC TYPE OF SLUDGE.

The usual sludge formation is due to an oxidation process of the attackable constituents of mineral oils[4] taking place most rapidly adjacent to the warmest parts within the transformer. Minute resinous bodies are first formed on the upper parts of the coil. These bodies accelerate the formation of more sludge which may attach itself to the coil, thereby slowly building up a deposit




Porous asphaltic sludge (mag. 1.1 dia.) of high molecular weight. It fuses above 300°C.

of such thickness that the heat from the coil is dissipated with difficulty. Not only are minute resinous bodies deposited upon the coils, but oxidation is carried on within and at the boundaries of the sludge. The oil readily dissolves approximately 15 percent of its volume of oxygen at operating temperatures. If the oil is not entirely free from suspended particles, these also tend to act as

[4] Cir. Bur. of Stds. No. 99, p. 11.

oxygen carriers. The initial deposit is soft, but the constituents gradually turn into a porous hardened mass.

Examination of a broken-down transformer containing deposited sludge showed that electrical breakdown had occurred where the deposit was the heaviest. After removing the deposit, it was washed with light naphtha and then thoroughly extracted for a day with petroleum ether. The light brown residue remaining on the Soxhlet thimble was completely honeycombed and very brittle.

The structure of the material (See Plate I) indicates the important role that heat plays in the formation of this oxidation product of the hydrocarbon. Numerous passages are threaded sponge-like throughout the mass where oil may be slowly circulated by convection currents. The finer holes gradually fill with sludge in the first stages of formation. This component is loosely adherent and may be removed by shaking thoroughly with petroleum ether.

Examination of the sludge showed that it consisted largely of hydrocarbons of high molecular weight containing oxygen. Thus, it may be considered a combination of oxyasphaltic compounds. The following table shows the loss by weight of the asphaltic sludge upon treatment with organic solvents:

ASPHALTIC SLUDGE EXAMINATION.

| | Wt. Loss Percent |
|---|---|
| Extraction of major portion of oil by shaking with light naphtha and drying. | |
| Six hours additional Soxhlet extraction petroleum ether at B. P.. | 12.3 |
| Twenty-four hours additional Soxhlet extraction $CCl_4$ ..... | 30.8 |
| Twenty-four hours additional Soxhlet extraction $C_6H_6$ ..... | 11.8 |
| Total amount extracted after washing with naphtha..... | 54.9 |
| Residue remaining was very brittle and porous. | |
| Heated in open tube gave oil, water and cracked products. | |
| Digestion with caustic attacked and dissolved most of the remaining residue. | |
| The residue fused above 300°C. | |

No free carbon was found indicating that cracking due to heat or electrical breakdown had not taken place. Thus through a process of oxidation (with or without accelerators or catalysers), polymerization and agglomerization a sludge was formed and deposited upon the active parts. Such sludge, though possessing desirable electrical properties, has a low coeffi-

cient of heat conductivity, thereby causing undue heating with a tendency to local hot spots and early electrical breakdown.

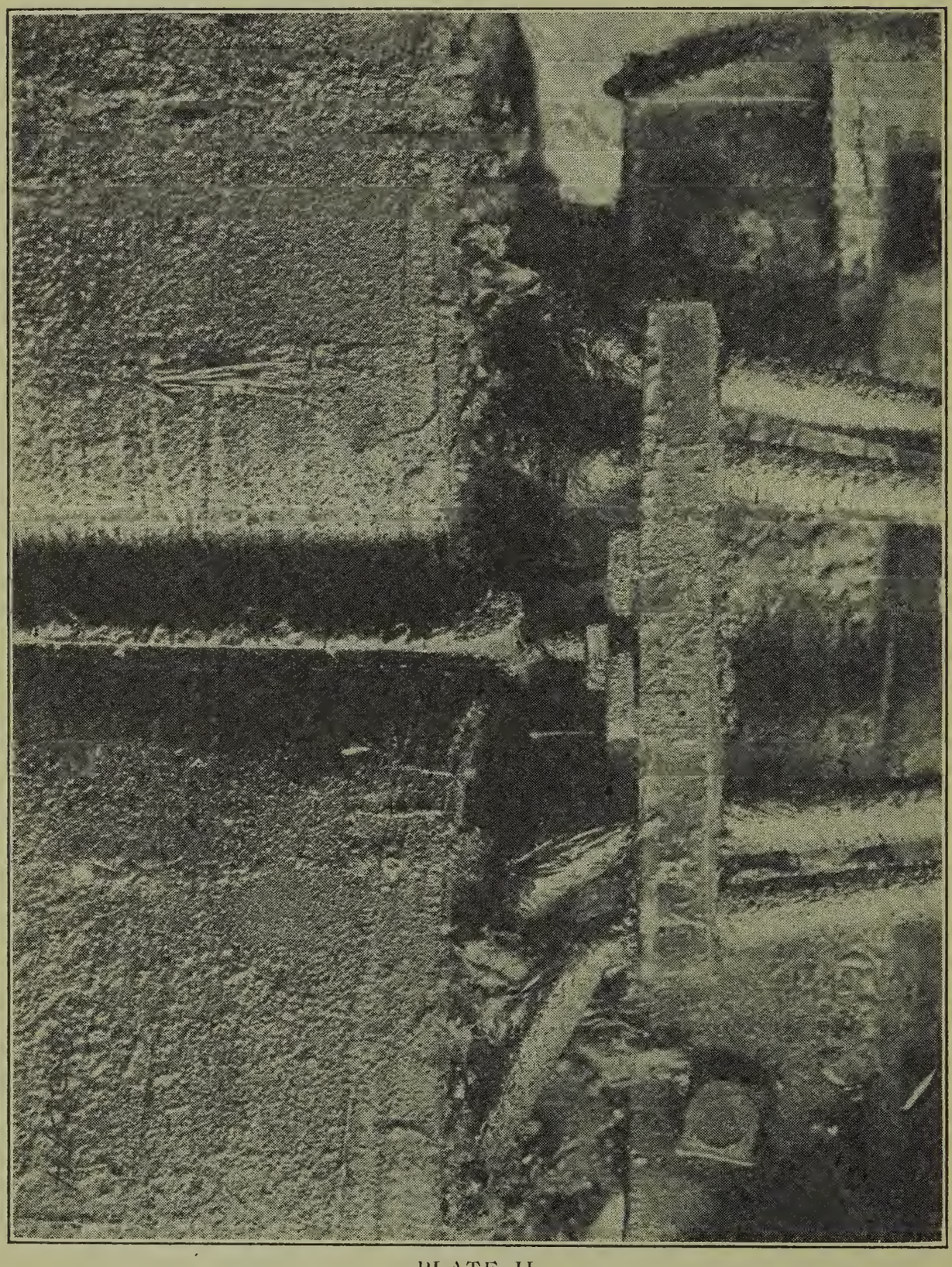


PLATE II

Section of transformer coil showing deposit of sludge in first stage of formation

In making life tests of certain small transformers, operating at 50 percent overload during the testing of various grades of oils, a striking difference in the sludging rate was noted. Plate II

shows how small deposits form upon the warmer sections of the working parts when using a viscous oil (Saybolt 90 sec.) which was highly unsaturated. This deposit was formed in less than a month's time, whereas other transformers showed less deposit after years of operation with a better refined oil.

## SOAP TYPE OF SLUDGE.

Another kind of deposit, quite different from that of the asphaltic nature described above, is frequently found in transformer oil and may be a source of much trouble. This kind of sludge usually appears as a yellowish to dark brown precipitate which is finely dispersed as flakes throughout the oil, convection currents materially aiding its dissemination. The formation of this type of sludge is very slow and occurs after the transformer has been in operation for some time. It settles slowly after many hours of standing to the bottom of the transformer tank, or is deposited in the quieter interstices. It may even collect, together with some asphaltic residue, as a slimy coating upon the cooling coils or the cooler parts of the transformer. It is partially soluble in oil, hence may soon reappear as a precipitate after the careful filtration of the oil through the oil-filter press containing blotting paper in the leaves. This kind of sludge has a very low insulating value compared with the strictly oxy-asphaltic sludge of high dielectric strength, typical of the first class.

The *light brown sludge,* of low dielectric strength, is a combination soap sludge with some oxidized hydrocarbon residue containing a very high percentage of moisture. The approximate analysis of the filtered sludge gives 96.6 percent water and only 3.4 percent of dry sediment. This would closely approximate a bar of water with a little soap, suspended in oil, instead of the usual bar of soap with a small water content. Extraction of the sediment with alcohol gave 51.9 percent soluble portion. Of the soluble part in alcohol, further analysis showed no heavy sulphide metals, no calcium oxide and only 3.2 percent of iron as $Fe_2O_3$. The undissolved portion, or 48.1 percent of the sediment, upon treatment with nitric acid, gave 20 percent of $Fe_2O_3$ and 3 percent

of CaO. In the following table the average analysis of the dried sediment is given.

TABLE I.

| | Percent. |
|---|---|
| $Fe_2O_3$ | 11,3 |
| CaO | 1.4 |
| MgO | 4.1 |
| Na and K salts | 13.0 |
| $H_2O$ Organic Material | 70.0 |

$SO_3 = 5.8$ percent.

A highly refined transformer oil dissolves about $2.2 \times 10^{-4}$ percent of water. During "breathing" of the transformer, humid atmosphere in contact with metal and oil surfaces condenses small quantities of moisture, which may be taken up more readily by impure oil. The better refined oil does not hold water in suspension, but allows it to settle to the bottom of the tank where a quantity of water may accumulate without transformer breakdown. If any soap sludge is present, the moisture content of the oil is raised. Dust particles, minute asphaltic bodies and any form of suspended matter in the oil tend to act as moisture carriers through adsorption or by means of nuclear condensation. Particles capable of being charged, especially in the electric field of the transformer act as carriers of oxygen and moisture, which are two of the most undesirable impurities in oil.

Certain complex organic acids[5] high in oxygen, as $C_{12}H_{22}O_{21}$, as well as fatty acids of the general formulæ,[6]

$$C_n H_{2n+1} COOH \quad \text{or} \quad C_n H_{2n} O_2$$

are derivatives of the hydrocarbon oils and may be formed under favorable oxidizing conditions. They interact slowly with metals and oxides to form soaps. Analyses of the various materials entering into transformer construction show that various oxides are present. Fuller board contains about 85 percent volatile hydrocarbons, 9.4 percent fixed carbon, a small quantity of moisture, silica, alumina, magnesia, sodium and calcium salts. The slight amount of moisture in oil assists in the formation of metal oxides such as rust. Fillers and driers in varnishes as well as other loading materials, contain various com-

[5] Z. angenwandte Chem. **31**, 69-70; Jor. Soc. Chem. Ind. **37**, 362A.
[6] Bernstoff Chem. **1**, 70-85.

pounds which may assist in the formation of soap sludge. Unprotected copper greatly accelerates sludge formation.

### THE CARBON TYPE OF SLUDGE.

A third type of sludge distinctly characteristic of electrical breakdown may be present in transformer oil. Corona discharge or arcing within the oil, breaks down the oil to amorphous carbon, saturated and unsaturated members lower in the series, and to various gases consisting mostly of $H_2$ (60 percent), unsaturated gases (20 percent), $CH_4$, CO, $CO_2$ and $N_2$. High voltage and low current discharge gives very finely divided carbon, whereas low voltage and high current produces comparatively large particles of carbon sludge. The finely divided sludge or precipitate is nearly pure amorphous carbon having a high specific resistance. The coarser precipitate contains much free carbon with small amounts of hydrocarbons low in hydrogen. Its specific resistance is lower than amorphous carbon. No graphite carbon was found as a result of electrical breakdown within the oil. However, if an arc plays near the surface of the oil where atmospheric oxygen is present "graphitoidal"[7] carbon is formed. This form or these forms of carbon are more conducting than amorphous carbon and lie somewhere in the series between the amorphous and graphite carbons. Some forms contain oxygen in small proportions suggesting an acidic character.

### GOOD OIL INHIBITS SLUDGING

By the judicious selection of a mineral oil which has been highly refined and is essentially saturated paraffine and cyclo naphthenes, one may obtain an oil which will give satisfactory performance in the carefully designed and well-cleaned transformer. If the oil is exposed to humid atmospheric conditions, it should be given a thorough filtration through an oil-filter press containing leaves of blotting paper and finely crushed, air-slacked lime. This procedure takes out sludge particles and water, and sweetens the oil, thus inhibiting the formation of the soap type of sludge. With the usual well-designed transformer and clean oil of high dielectric strength, no carbon type of sludge can be formed, unless a heavy breakdown surge is allowed to enter the transformer.

[7] Name suggested by H. C. P. Weber. Westinghouse Electric & Mfg. Co., Pittsburgh, Pa.

### CONCLUSION.

Three general types of transformer oil sludges have been briefly described. The first type, or asphaltic nature, is an oxidation and polymerized product of attackable oil. It is the most general form of sludge. It collects upon the active parts of the transformer, thus preventing the dissipation of heat. If moisture free its electrical properties are fairly good. The second type, or soap sludge, is a good moisture and oxygen carrier. It forms slowly and it is difficult to remove entirely by filtration. The carbon type of sludge is due to electrical breakdown.

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## DISCUSSION.

W. S. Moody[1] (*Communicated*): Mr. Rodman's paper clearly sets forth the various causes for oil sludging, and, as there has not been a great deal of publicity on the subject, the paper is timely.

During the first ten years or more during which oil was used as an insulating and cooling medium in transformers, cases of serious sludging were quite common, and of necessity considered more or less a mystery. The subject, however, soon received the best attention of the electrical engineers and the oil manufacturers, and their efforts finally resulted in much better oils, which, as Mr. Rodman explains, have now been available for some ten years or more, and in improvements in the design of transformers, in accordance with which local hot spots are carefully avoided.

It should be pointed out, however, that it is not practical for either the electrical manufacturer or the customer to test all oil that is used, to see that each lot is free from sludge-producing materials; also that there is not a definite temperature, below which no sludging takes place and above which serious sludging occurs; also that emergencies may often arise which justify the customer operating his transformers above the designed operating temperature, and thereby cause sludging of an oil that would not sludge under anticipated conditions of operation.

[1] Chief Engr., Transformer Dept., General Electric Co., Pittsfield, Mass.

In other words, with the best available sources of oil, and with excellent electrical design in the transformer, there is still some chance of sludging beginning, and, as Mr. Rodman points out, sludge acts as a catalytic agent to produce more sludge at lower temperature than was necessary to start the first sludging. Therefore, it is desirable, especially in large units used in important service, to have some additional safeguard against sludging.

Such a safeguard is effectively found in the use of a transformer tank construction that prevents the atmosphere from coming in contact with the hot oil, thereby avoiding in the most direct way the action which Mr. Rodman properly says is a direct oxidation process, except for the third class of sludge, which results from actual breakdown of the oil due to the presence of corona. This, of course, should never be encountered in any well designed transformer.

We first experimented with tanks constructed in this manner six years ago, and found that necessary mechanical construction could be readily carried out, and that the results were practically complete avoidance of sludging under any temperature that would be allowable from the standpoint of insulation deterioration. Since then we have produced some 1,250,000 Kva. of transformers, and 275 units incorporating this construction, and have yet to observe a single case of appreciable sludging in any of them. The construction not only prevents sludging in this effective manner, but is also an excellent one in that it gives the operator immediate indication of any leak in the tank through which moisture might enter if the static head of oil were not maintained.

C. F. Roth[2]: On page 104, I would like to ask where the sodium and potassium salts are derived from?

C. J. Rodman (*Communicated*): Mr. Moody's discussion is interesting. His success in experimentation with transformer tanks where the oil is kept out of contact of air by completely filling the tank with oil and using an overflow system is commendable, thus proving a good way to retard the sludging rate of the oil. Inasmuch as some difficulty in practice has been experienced in making tight metal joints to prevent leakage of oil, it would seem to be more advisable to maintain an inert gas space above the oil. Experiments along this line have been successful.

[2] New York City.

A transformer tank completely filled with oil is objectionable, inasmuch as a serious disruption of the tank would occur if a power arc were formed within the transformer, perchance upon failure of a circuit breaker. It has been shown in our experiments that approximately 85 cc. of gas is liberated per Kw./sec. of energy dissipated in the arcing of the oil. Oil is practically non-compressible, hence something would speedily give way. An inert gas space acts as a cushioning effect for the steep wave form gradient of an arc rupture of the oil, and simultaneously reduces the fire hazard connected therewith.

In answer to Mr. Roth's question, I would like to state that the sodium and potassium salts, especially the former, are found in the soap sludge as the analysis shows. They are derived from the fullerboard spacing materials, the impregnated insulating compounds, and to a much lesser degree from the paints and varnishes used. A very small amount of these salts, as pointed out in the paper, enter into the composition of the soap sludge.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# FACTORS INFLUENCING THE ELECTROLYSIS OF ORGANIC COMPOUNDS.[1]

By Raymond Freas[2].


## Abstract.

A contribution attempting to encourage further research and study of organic compound electrolysis. The discussion, limiting itself to electro-reduction processes, states that the concentration of a "depolarizer" relative to that of active hydrogen or $H^-$, as well as $H^+$, determines the nature of reduction possible. The factors influencing the relative velocities of reaction are enumerated and in spite of their great number the author maintains it possible to secure selective reduction electrolytically. An experimental arrangement used, and adaptable to continued study, is presented. [A. D. S.]


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The application of electro-chemistry to organic chemistry is not new, but is comparatively undeveloped. Even considering the abundance of the literature on the subject, especially the German, many phases of it are inadequately studied experimentally. There are no lack of hypotheses to account for the phenomena of electrolysis, but exhaustive study of these phenomena to give quantitative expression to them has not been systematically carried out. It is one of the purposes of this paper to attempt to arouse a greater interest in this experimental study of electrolysis as distinguished from its study in direct relation to a successful industrial process where costs and other practical considerations so largely determine limits of investigation.

Many fascinating problems offer themselves for solution, problems which must yield data of the greatest value to solution of

[1] Manuscript received June 22, 1921.
[2] Research Chemist, New Orleans, La.

the problems arising in applied electrochemistry. A simple discussion of the most important factors entering into electrolytic reduction, with some mention of points of possible interest to the investigator, may be timely. For purposes of simplicity the discussion in this paper will be limited to electro-reduction processes.

Practically nothing is known of the mechanism of the discharge of ions in electrolytes at platinum electrodes. The older effort to explain hydrogen gas evolution at the cathode either dodges the issue or simply states that the active hydrogen is in the atomic state due to the ions giving up their charges at the cathode. It would seem a preferable view and one more susceptible of proof to assume that $H^+$ gains not only one electron but a second one becoming $H^-$, and in that state of instability is in a highly active condition, ready to enter into any reaction which will tend to restore its equilibrium, whether this be simple union of

$$H^+ + H^- \rightarrow H_2$$

or action on a depolarizer to cause its reduction

$$C_6H_5NO_2 + 4H^- \rightarrow 2H_2O + C_6H_5NH_2$$

This view would explain the phenomenon of excess potential as the reverse E. M. F. set up by the layer of $H^-$ on the cathode towards the opposing layer of $H^+$ at the cathode. An organic substance which is capable of electrolytic reduction is called a "depolarizer." Upon the concentration of a depolarizer relative to the concentration of active hydrogen or $H^-$, as well as that of $H^+$, will depend the stage of reduction attainable as well as the amount of reduction possible with a given experimental set-up. In other words, the relation of the velocities of the reactions

$$H^+ + H^- \rightarrow H_2$$

and

$$\text{Depolarizer} + nH^- \rightarrow \text{Reduction Product} + (n/2)H_2O$$

will determine the nature of the reduction. All factors which bear upon these velocities are then of the utmost importance, and will be discussed in the succeeding paragraphs.

Of all the factors influencing electrolytic reduction, the most important is probably excess potential. This may be defined

again as the reverse E. M. F. set up by the layer of $H^-$ on the cathode towards the opposing layer of $H^+$ at the cathode. This excess potential varies with the metal chosen, the physical condition of the latter, the temperature, and the current density. The extent of this potential is one of the two great determining factors of the direction and the energy of an electrolytic reaction, the other being the total electrode potential. Most of the other factors to be taken up in order are of interest indirectly according to their effect in increasing or diminishing the excess potential. A most interesting problem would be found in a careful investigation of the excess potential of all the commoner metals, alloys, and other electrode materials such as carbon, lead peroxide, copper sulphide, etc. The older values given in the literature would be rendered more useful by a checking up, and the addition of values as yet undetermined. Further, the effect of varying temperature, concentration of electrolyte, current density and other factors, on these values would constitute an important contribution.

The accepted explanation of the cause of the different excess potential values for hydrogen with different metals is the varying catalytic power they exhibit towards the reaction

$$H^+ + H^- \rightarrow H_2$$

Thus platinized platinum will catalyze it very powerfully, polished platinum less so, and less and less the following metals in the order given: iron, gold, silver, nickel and copper, while with lead and mercury the catalysis is so slight as to allow the accumulation of a large concentration of H, hence extremely energetic reduction results from the use of the latter two metals. The variation in excess potential of the same metal seems intimately connected with the physical character of the surface. Thus platinized platinum, where the surface exposed is far greater than with polished platinum of the same apparent surface area, exhibits a smaller excess potential than the latter. This opens up the possibility of the measurement of excess potential as a means of control of the physical character of metals in their practical preparation on a large scale. Such a possibility would depend, of course, on the assumption that the surface structure of the metal is essentially the same as that of the interior. Cor-

rosion tests which are so important in the study of metallurgy, might be paralleled by excess potential measurements with the yield of very important data. Our knowledge of electrolysis would be much advanced by a more exhaustive study of the phenomena of excess potential.

Excess potential is also very much affected by the presence of the smallest traces of foreign metals as impurities. Study of reactions is useless without taking the greatest pains in the preliminary treatment of electrodes to insure the absolute purity of their surfaces at least.

Electrode potential is the other of the two most important factors. It is so indissolubly connected with current density that they will be considered together. The determining factor as to whether a given reduction will take place or not is the electrode potential. We are all familiar with the separation of metals from a mixed solution by a gradation of potential at the cathode. As this is increased, a point is reached where the metal having the lowest potential value is completely deposited, whereupon the one next higher in value begins depositing. In similar manner each reduction has a definite potential at which it begins to take place and a higher at which a more advanced stage begins, if such is theoretically possible, so by controlling the electrolysis within the proper limits of potential, we may closely regulate the reaction. From this we may see that it is of the utmost importance to make frequent measurements of the potential of the active electrode during an experiment. The most illuminative information is thereby gained. Practically such measurements are somewhat difficult to make, so the current density, which is directly dependent upon the former, and which is itself very easy of measurement and equally easy of control, is chosen instead as a guide.

The current density may be defined as the current strength, in amperes, per unit electrode surface, in square decimeters. Its regulation is most conveniently accomplished by the insertion of the necessary external resistance, but may also be altered by the variation in the size of the electrode as well as by the choice of the proper concentration of electrolyte. For a given range of current density within which a given reaction will take place,

the greatest current efficiency will be obtainable at the lowest end. At the higher end more current is consumed in the production of hydrogen gas and in heat which reduces the efficiency considerably at times. Also the heat produced by high current densities is so great that some cooling device is frequently required for proper reduction. The current density as a means of experimental control is well exemplified by the reduction of nitrobenzene to azoxybenzene[3] and the further reduction to azobenzene[4] and hydrazobenzene[4].

At this point it might be well to give a table of the more important factors before further discussion of them individually, and then treat them in their relation to one another.

FACTORS INFLUENCING ELECTROLYSIS.

*Regular*

Variable

1. Excess Potential
2. Electrode Potential and Current Density
3. Temperature

Non-variable

1. Concentration of Electrolyte
2. H Concentration
3. Concentration of Depolarizer
4. Electrode Metal
5. Physical Condition of Metal
6. Depolarizer Solubility
7. Stirring.

*Special*

1. Reaction of Electrolyte with Active Electrode
2. Shape and Relative Position of Electrodes.
3. Cell Construction
4. Added Colloids
5. Carriers
6. Evaporation
7. Foaming
8. Relative Osmotic Pressure of Anolyte and Catholyte
9. Impurities (including effect of "Poisons")
10. Diaphragm
11. Deposits upon Active Electrodes
12. Side Reactions at Anode (in oxidation, such as sulfonation).

Such a classification as the above is of necessity quite arbitrary. The division of the regular factors into variable and non-variable

[3] Chem. Zeit. **17**, 210.

[4] Zeit f. Elektrochemie **5**, 108.

is especially so and refers of course, to variation after the beginning of an experiment when choice has been made of metal, concentrations, etc. Its only use is as a basis for discussion.

The next factor in order of importance is temperature. A given reaction usually has for a given experimental layout, a definite range of temperature within which only will it take place. For example, I attempted to carry out a reduction of a compound containing a CO= group, using first platinum, then copper and aluminum to no purpose. On using a mercury cathode the reduction went beyond the desired stage. It was found necessary to resort to cooling and holding the solution at about 0° to get smooth and efficient reduction. The general significance of temperature does not essentially differ from that in ordinary chemical reduction.

The nature of the electrolyte and its concentration depend on the effect desired. Most electrolytic reductions are carried out by means of the use of an electrolyte as conductor, and a dissolved or emulsified depolarizer, which is not a conductor, added. In the choice of the electrolyte many things are to be considered. For instance, whether an acid, base, or salt is selected depends upon whether a large, small, or medium $H^+$ concentration is required, further whether high, low or medium conductivity is desired. Sometimes a very constant reactivity of the solution is obligatory, in which case a buffer mixture is used, or acid or base added as needed during the experiment. Sodium acetate and acetic acid, and sodium carbonate and bicarbonate are examples of such buffer mixtures.

The concentration of the depolarizer is significant in that its proper balance with the $H^-$ concentration is essential to good current efficiency. Depolarizer solubility is one of the most frequent causes of trouble in electrolytic reduction. It is often very difficult to choose an electrolyte which will be suitable for maintaining the proper reaction, and at the same time be capable of dissolving a sufficient quantity of depolarizer. Upon the solution of this difficulty will depend the success or failure of many an experiment. The use of fine suspensions, or emulsions of liquid or solid is of practical value, but of none in studies of the nature suggested in this paper, where a knowledge of active concentra-

tions is of the greatest importance. Mechanical stirring is of the greatest use in maintaining proper concentrations at the active electrode and is practically a necessity in theoretical investigations.

Many special factors may enter into our experiments. The reaction of the electrolyte with the electrode is of more importance in electrolytic oxidation than in reduction. It is often important in the latter also, particularly with solutions of great acidity. Cell design, relative size and shape, and situation of electrodes should be as simple as is compatible with the requirements. The bearing of most of these special factors is so obvious that mere mention of most of them will be sufficient. Colloids when added to the electrolyte sometimes exert an influence towards smoother progress of the reaction. The reason is unknown and their choice is entirely empirical. Carriers are used in many experiments. Here we are really using chemical reduction or oxidation, the latter usually, and employing the current as a means of regenerating the spent liquor. Evaporation enters into our calculations when one of the substances, whether solvent, depolarizer, or reduction product is volatile at the temperature of the experiment. Foaming interferes sometimes and the remedy is either the use of a lower current density, if that be possible, or by coating the surface of the solution with an inert antifoam liquid such as albolene. The appearance of foaming may usually be taken as a sign that the current density is too high and that the current efficiency will be quite low due to current consumed in hydrogen gas production. The relative osmotic pressure between the anolyte and catholyte is of importance only where it becomes great enough to bring about a noticeable change of volume of the solutions in the cell compartments, due to the diffusion set up by the pressure. In some of my experiments of long duration, this became a serious interference and had to be corrected by adjustment of concentration of the solutions in the anode and cathode compartments.

Action of strong electrolytes on the diaphragm occasionally occurs, and in such a case a choice of a different material for its construction is required. It is always desirable but seldom possible where high efficiency is sought, to use an undivided cell. The majority of electrolytic processes employ a diaphragm of

ordinary porous ware, one of the several patented silicious materials such as "electro-filtros" or perhaps asbestos cloth.

Infrequently a deposit of an insoluble substance upon the electrode occurs. This is exemplified by the separation of sulphur on the anode when an electrolyte of sodium sulphide or hydrosulphide is used. This may lead to a greatly increased resistance and upset the smooth progress of the electrolysis.

Another infrequent occurrence is the case of a reaction interfering with the principal and desired one of reduction. This is well illustrated by the occurrence of sulfonation in the preparation of paraminophenol[5]. In that process sulfonation takes place to an interfering degree except between a special range of concentration, 80 to 96 percent, of the sulfuric acid used as electrolyte.

The influence of impurities has already been taken up in the discussion of its effect on excess potential where its influence is most marked. The impurities that interfere most are small amounts of metals. In electrolytic processes the materials used must be of the purest. This fact has had an influence in retarding the adoption of such methods. The principal cause of this backwardness is our lack of exact knowledge. Another is the comparatively high cost of the original installation of cells, generator, etc. The power cost is not the item it may seem on first thought, when compared with the relatively high value of most of the products obtained by these methods.

Although the discussion in this paper has been confined to reduction, the same general principles may be applied to the study of oxidation, halogenation and substitution processes. These offer greater complexity, and on this account the development of our knowledge concerning them as well as their practical application to organic industry has been slower. In their case we have the discharge of ions at the anode and the formation of such active ions as $OH^{+}$, $Cl^{+}$, $SO^{++}_{4}$, $NO^{+}_{2}$, etc., and these active ions oxidize or substitute the depolarizer. Some of the complexity here is due to the fact that we have a very large number of anions possible, compared to the comparatively few cations.

In addition to the problems suggested in the discussion of the

[5] Ber. 26, 1846.

factors entering into electrolysis, the following might be offered: A study of electrolytic reduction, under constant conditions, of compounds containing a definite group, for instance $CHO^-$, in several normal members of an homologous series, such as the aliphatic aldehydes. This could be varied by choice of various hydrocarbon radicles joined to $CHO^-$, such as an aliphatic, an aromatic, and a terpene aldehyde. A study of the requirements of efficient reduction of these compounds should throw much light on the energy needs of their reactions, also upon the influence of a given group upon the ease or difficulty of a reduction. A measurement of the potential drop caused by the addition of a definite concentration of the depolarizer, say tenth molar, over that of the visible evolution of hydrogen gas should give interesting comparative values which would approximately express the energy requirements of the reactions. This is not strictly true due to losses from heat developed as well as loss due to gas evolution. However, when minimum potential necessary to the reaction is used and the heat loss calculated, we can obtain data of the reaction energies which would be quite reliable. A mere measurement of the potential difference across the cell terminals is of doubtful value, however useful it may be in figuring power efficiency of a practical process.

Another line of research offering interest would be a study of the possibilities of conducting an electrolytic reduction and oxidation simultaneously. I know of no instance where this is done and it is, I believe, considered almost impossible to do it practically.

In much of the published work on organic electrolysis done from the standpoint of pure research as contrasted with the carrying out of an industrial process, there is a very insufficient record of data given which would be of the greatest assistance in enabling one to use the author's findings. Some of this lack is due to carelessness or inattention to detail. For the most complete information we may want much or all of the following data:

1. Watt Hours Consumed.
2. Ampere Hours Consumed.
3. Periodic Measurements of Electrode Potential.
4. Periodic Measurements of Temperature.
5. Periodic Determinations of Yield of Reduction Product.

6. Periodic Measurements of H Concentration.
7. Current Density (Current usually is kept constant).
8. Molar Concentration of Electrolyte.
9. Molar Concentration of Depolarizer.
10. Dimensions, Material, Shape, and relative Position and Distance apart of Electrodes.

The measurements of electrode potential are plotted against ampere hours consumed and show breaks in the curve which are very illuminative in the information yielded. For instance the completion of one stage of a reduction and the beginning of another is usually accompanied by a rather marked break in the curve. Further, the current applied may be gradually increased and when plotted with the potential measurements also shows many points of interest.

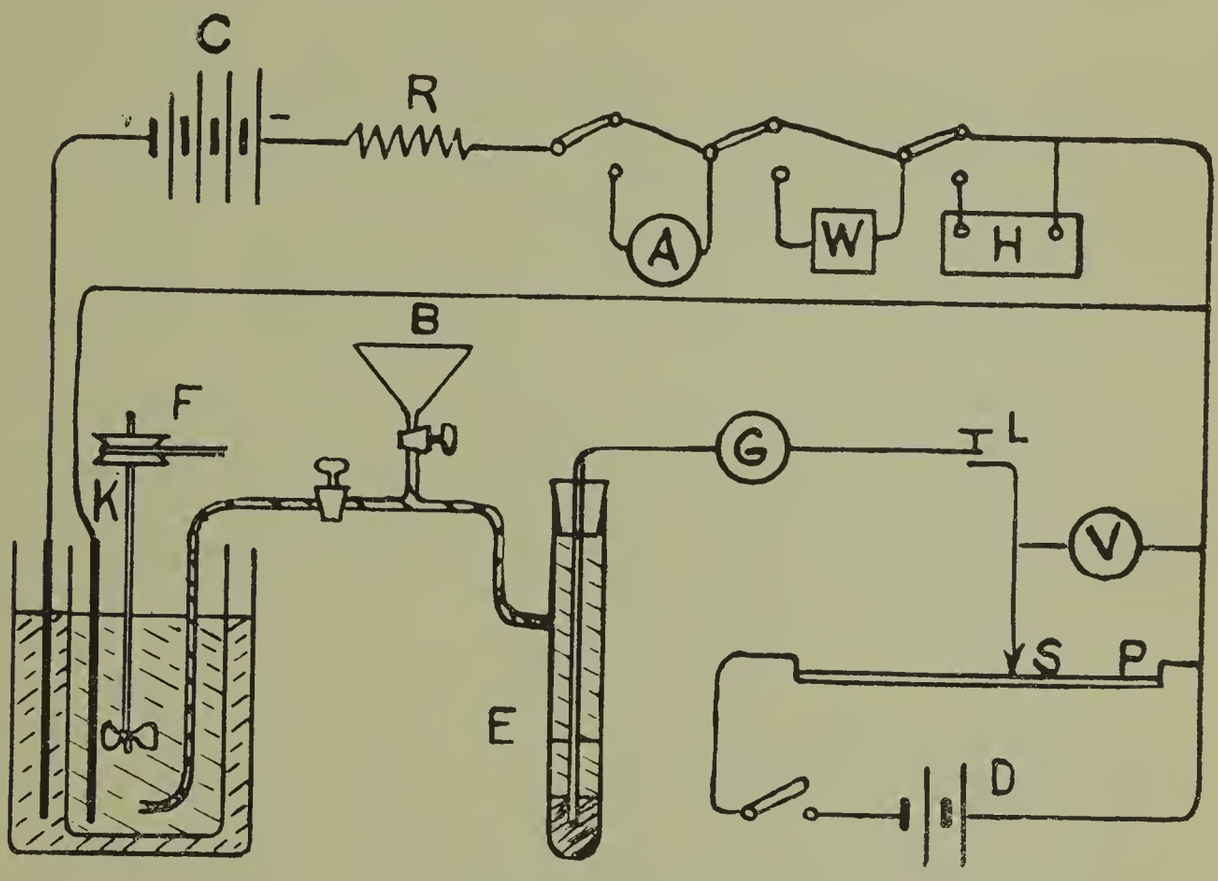
In spite of the great number of factors requiring attention and control, it is possible to obtain a rather fine adjustment of these, and so carry out selective reduction which would be difficult or perhaps impossible by the usual chemical methods. The product obtained by electrolytic methods is usually purer, and less trouble is had in its subsequent handling. In some cases the product separates as a precipitate and may be removed either during or after the completion of the reaction. As to what compounds can better be produced by electrolytic methods than by the usual chemical means, the reader is referred to an excellent paper by Thatcher[6]. This author concludes that those substances having the highest "form value", that is whose value is due principally to the work expended upon them in their preparation, rather than on the high cost of the raw materials entering into their manufacture, are those most susceptible of preparation by electrolysis. The greater cleanliness of these methods and the usually greater purity of the product are much in their favor.

A convenient experimental arrangement for such studies as are herein suggested is illustrated and described below. It has been in use by the author with a few variations, for several years.

The current source, C, is usually a number of storage cells, two to ten in number, connected in series, or a motor generator set. The negative lead from this source passes through a resistance, R, variable from about one to one hundred ohms, so wound as to safely carry the maximum current used, which is seldom

[6] Trans. Am. Electrochem. Soc., 1919, 36, 337.

more than ten amperes. From this it passes through an ammeter, A, reading to 10 amperes in tenths, then into a watt hour meter, W, capable of recording 500 watt hours in watt hour units. Next in circuit is a constant current controlling device, H, which should be able to keep the current constant to one or two tenths of an ampere. These last three instruments are provided with shunting switches arranged so as to permit their re-




C Current Source
R Resistance
A Ammeter
W Watt Hour Meter
H Constant Current Relay
K Cathode
F Mechanical Stirrer
B N/Acid Reservoir
E Calomel or $Hg_2SO_4$ Electrode
G Galvanometer
L Galvanometer Key
P Potentiometer
S Sliding Contact
D Reference Potential
V Voltmeter

moval from the circuit when not required, without interrupting the current. From H the current passes to the cathode, K, of the electrolytic cell, and also to a terminal of the potentiometer bridge, P. From this point to a terminal of the potential reference cell, which may be either one or two dry cells in series, or other low internal resistance cell of invariable E. M. F. The other terminal of this reference battery is connected through a cutout switch to the other terminal of the potentiometer bridge. The sliding contact of the latter leads to the galvanometer key,

K, thence to the galvanometer, G, and next to the calomel or other reference electrode, E. This is connected in the usual manner to the cathode compartment by tube of small diameter. F is a mechanical stirrer and B a funnel with stop-cock which permits the above tube to be flushed occasionally with the solution used in the reference electrode and thus prevent its contamination. Between S and the right terminal of bridge is shunted a high resistance voltmeter which permits of direct voltage readings. This should read to 2 volts in hundredths. It is difficult to obtain a watt hour meter which will be suitable for this layout. When the necessary balance between the cathode calomel potential and the equivalent potential on the bridge is obtained, a simple pressure of the voltmeter button will give the direct voltage reading. This gives much greater simplicity in the making of these readings than is possible with the more accurate method used in hydrogen ion concentration measurements.

The reader may refer to the direct references following, as well as the other general references and text books for much helpful information in their study of electrolytic reduction and oxidation of organic compounds.

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## DISCUSSION.

C. J. THATCHER[1]: I found one could get much better oxidation processes with negatively, than with positively, charged electrodes; that is, if one polarized the electrode negatively before using it for oxidizing. Whereas, if you gave it initially a positive charge one got very different results.

ALEXANDER LOWY[2]: I would like to say that whoever looks upon electro-organic chemical methods as of minor importance is making a great mistake. I do not know to what extent some of these methods will be commercialized, but there will be a great deal of important work done in this field. I have a paper that concerns this particular topic, *viz.*, the electrolytic oxidation of the leuco base of malachite green to the color base. This work has been done, of course, on a small scale, and provided the details are worked out for large scale production, it may be operated on a commercial basis. It is a question of oxidation. We tried to oxidize the leuco base to the color base by different oxidizing media. Ozone or hydrogen peroxide were not effective. We used liquid air to see the possible oxidation effect on the leuco base. When we used a lead peroxide anode in presence of a small amount of catalyst the oxidation took place at a slow rate, giving the dye as a product.

[1] New York City.
[2] Professor of Organic Chem., Univ. of Pittsburgh, Pittsburgh, Pa.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# ELECTROLYTIC OXIDATION OF THE LEUCO-BASE OF MALACHITE GREEN.[1]

By Alexander Lowy and Elmer H. Haux[2].

Abstract.

A tabulation of forty-four experiments, on the electrolytic oxidation of the leuco-base, is given. The conclusions arrived at indicate the necessity of a catalyst, an elevated temperature for efficient oxidation, a low concentration of the leuco-base in the anolyte, and sulfuric acid as solvent and electrolyte. The highest dye yield was obtained with uranyl sulfate as catalyst, platinum cathode, and nichrome gauze anode in dilute sulfuric acid solution, at a temperature of 85°C. [A. D. S.]

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The object of this investigation was to ascertain the possibility of substituting electrical energy for chemical energy in the oxidation of the leuco-base of malachite green.

The leuco-base was prepared according to the method described in Cain and Thorpe[3]. The leuco-base is usually oxidized, on the commercial scale, by a slight excess of the theoretical quantity of lead peroxide, which must be carefully prepared and used in the form of a thin aqueous paste. The insoluble lead compounds are then filtered, the filtrate heated, and the soluble lead salts precipitated with sodium sulfate. Equations for the entire process will be found on the following page.

In order to eliminate the use of lead peroxide and thereby the subsequent precipitation and filtration processes, electrolytic oxidation was used.

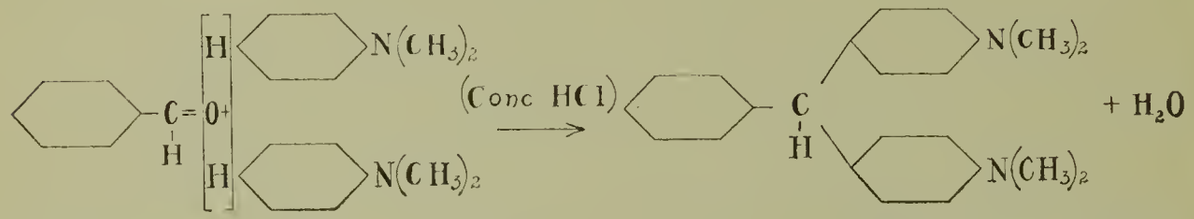
The apparatus used, is shown on page 125.

[1] Manuscript received July 15, 1921.

[2] Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

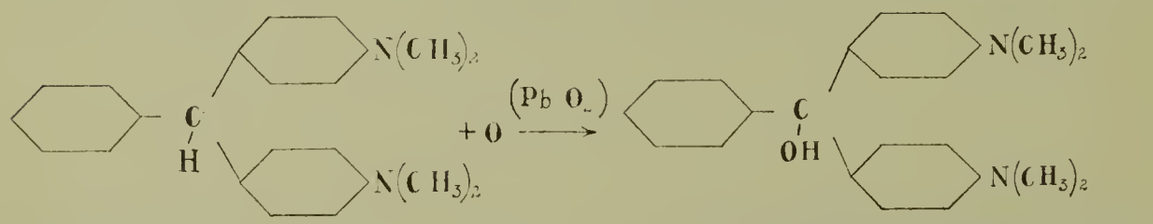
[3] "The Synthetic Dyestuffs and Intermediate Products."

In order to indicate the conversion of the leuco-base to the solid dye, experiment No. 43 is described, herewith, in detail. Ten grams of the dry leuco-base are suspended in 20cc of water. Then 17 grams of concentrated sulfuric acid, containing 0.1 gram of uranyl acetate, are added to the suspension, and the mixture boiled until a clear solution is obtained. It is now diluted to two litres and poured into the anode compartment of the cell. The porous cup is filled with an 8 percent solution of sulfuric acid and serves as the catholyte. The cell and contents at this point

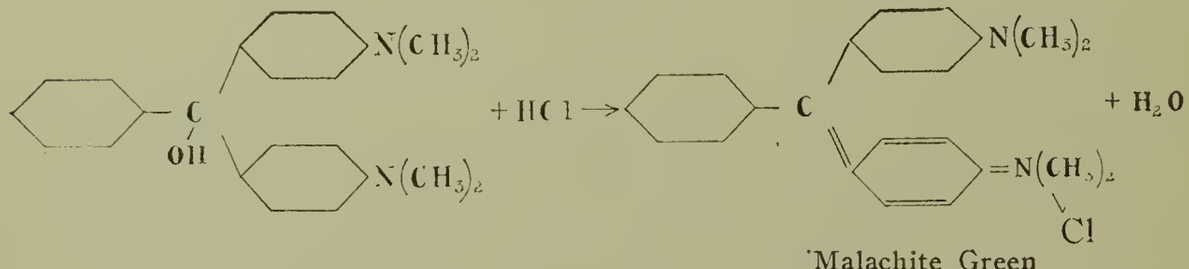



Benzaldehyde + Dimethyl aniline (2 mols.)

Tetramethyl-diamido-triphenylmethane (Leuco-Base of Malachite Green)



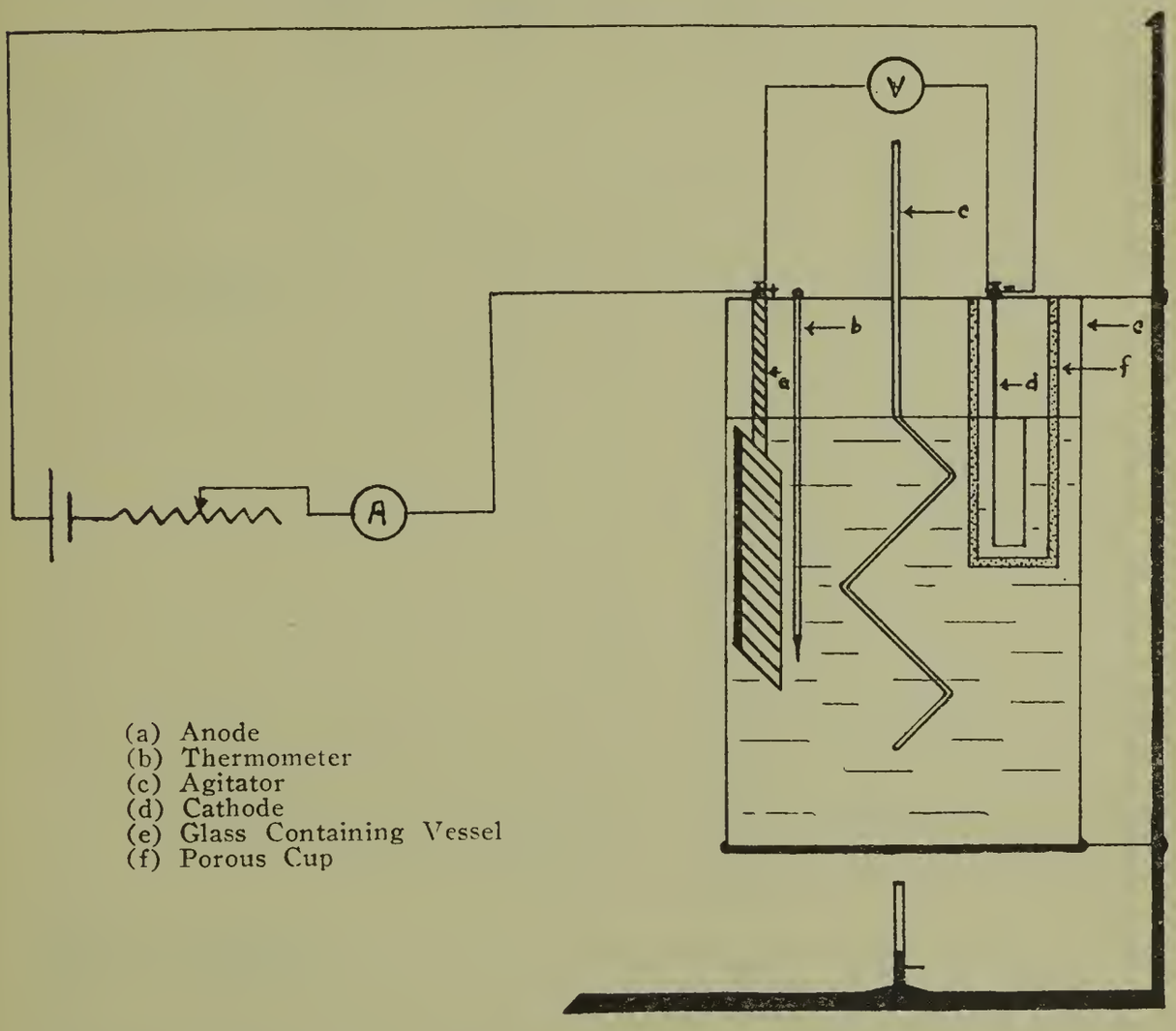

Color-Base of Malachite Green




Malachite Green

are raised to a temperature of 80°C. and maintained with constant agitation, throughout the operation. When the desired temperature has been reached, the electrodes are put into position. The anode consists of two lead plates each 1 sq. dm. area, upon which there is an electrolytic deposit of lead peroxide; the cathode is a cylinder of platinum gauze. The current used is one ampere, the potential drop across the terminals of the cell being 4.5 volts. The time required for complete oxidation is approximately three hours, after which the electrodes and porous cup are removed and the free acid in the anolyte neutralized with sodium bicar-

bonate or ammonia. This neutralization is necessary, since on cooling, in the presence of free acid, the structure of the dye undergoes a rearrangement with a consequent loss of material. After neutralization, the solution is filtered, and while stirring 15 grams of zinc sulfate and 150 grams of common salt added. The mixture is allowed to stand for 12-15 hours, during which the zinc sulfate salt of the dye separates out in a crystalline form and may be easily filtered. On the commercial scale the zinc chloride




(a) Anode
(b) Thermometer
(c) Agitator
(d) Cathode
(e) Glass Containing Vessel
(f) Porous Cup

salt of the dye-stuff is formed, but this is precipitated in a more or less tarry form which is difficult to handle even on a small scale. The yield, by the above method is 75 percent, gross, figured on the leuco-base used, but as its strength is only 75 percent of that of standard, the actual color yield is only 57 percent. The yield was worked up to 66 percent in successive experiments. The low yield is partially due to the small quantity of leuco-base employed, and it would seem that by operating on a larger scale the yield would be materially increased.

| Exp. No. | Vol. of Anolyte cc. | Wt. of Leuco-Base | Temp. °C | Time. hrs. | Amps. | Volts. | Solvent for Leuco-Base. |
|---|---|---|---|---|---|---|---|
| 1 | 600 | 1.3 g. | 20 | 3 | 0.175 | 4.1 | 5 g. $H_2SO_4$ |
| 2 | " | " | " | 4 | 0.025 | 2.0 | " |
| 3 | " | " | " | 6 | 0.5 | 5.8 | " |
| 4 | " | " | 85 | " | 0.2 | 3.3 | " |
| 5 | " | " | " | " | 0.5 | 5.8 | " |
| 6 | " | " | " | " | 1.0 | 4.5 | " |
| 7 | " | " | 20 | " | 0.6 | 0.75 | " |
| 8 | " | " | 85 | " | 0.6 | 0.75 | " |
| 9 | " | " | " | " | 1.0 | 4.5 | " |
| 10 | " | " | " | " | " | " | 7g. $CH_3COOH$ + 1g. sod. acetate |
| 11 | " | " | " | " | " | " | 7g. $CH_3COOH$ + 5g. HCl |
| 12 | " | " | " | " | " | " | " |
| 13 | " | " | " | " | " | " | 5 g. HCl |
| 14 | 2000 | 5 g. | 20 | 3 | " | " | 10g. $H_2SO_4$ |
| 15 | " | " | 85 | " | " | " | " |
| 16 | " | " | 20 | " | " | " | " |
| 17 | " | " | 85 | " | " | " | " |
| 18 | " | " | 20 | " | " | " | " |
| 19 | " | " | 85 | " | " | " | " |
| 20 | " | " | 20 | " | " | " | " |
| 21 | " | " | 85 | " | " | " | " |
| 22 | " | " | 20 | " | " | " | " |
| 23 | " | " | 85 | " | " | " | " |
| 24 | " | " | 20 | " | " | " | " |
| 25 | " | " | 85 | " | " | " | " |
| 26 | " | " | 20 | " | " | " | " |
| 27 | " | " | 85 | " | " | " | " |
| 28 | " | " | 20 | " | " | " | " |
| 29 | " | " | 85 | " | " | " | " |
| 30 | " | " | 20 | " | " | " | " |
| 31 | " | " | 85 | " | " | " | " |
| 32 | " | " | 20 | " | " | " | " |
| 33 | " | " | 85 | " | " | " | " |
| 34 | " | " | 20 | " | " | " | 25cc. $C_2H_5OH$ + 1g. sod. acetate |
| 35 | " | " | 75 | " | " | " | " |
| 36 | " | " | 20 | " | " | " | 15cc. benzene + 1g. $Na_2CO_3$ |
| 37 | " | " | 85 | " | " | " | " |
| 38 | " | " | 80 | " | " | " | 15cc. $CH_3COOH$ + 1g. sod. acetate |
| 39 | " | " | " | " | " | " | 10g. $H_2SO_4$ |
| 40 | " | " | " | " | " | " | " |
| 41 | " | 50 g. | " | " | " | " | 90g. $H_2SO_4$ |
| 42 | " | 100 g. | " | " | " | " | 160g. $H_2SO_4$ |
| 43 | " | 10 g. | " | " | " | " | " |
| 44 | " | " | " | " | " | " | 17g. $H_2SO_4$ |

| Exp. No. | Catalyte. | Cathode | Anode. | Size of Anode. | Catalyst. | Dye Yield. Percent. |
|---|---|---|---|---|---|---|
| 1 | same as anolyte | Pt | Pt | 1sq.dm. | none | none |
| 3 | " | " | " | " | " | " |
| 4 | " | " | " | " | " | " |
| 5 | " | " | " | " | " | trace |
| 2 | " | " | " | " | " | " |
| 6 | " | " | " | " | " | " |
| 7 | " | " | $PbO_2$ on Pb | " | " | none |
| 8 | " | " | " | " | " | trace |
| 9 | " | " | " | " | " | " |
| 10 | " | " | Pt | " | " | none |
| 11 | " | " | " | " | " | " |
| 12 | " | " | $PbO_2$ on Pb | " | " | " |
| 13 | " | " | " | " | " | " |
| 14 | 15g. $H_2SO_4$ | " | Pt | " | " | " |
| 15 | " | " | " | " | " | " |
| 16 | " | " | $PbO_2$ on Pb | " | 0.1g. $VSO_4$ | trace |
| 17 | " | " | " | " | " | 7 |
| 18 | " | " | " | " | 0.1g. $UO_2SO_4$ | trace |
| 19 | " | " | " | " | " | 55 |
| 20 | " | " | " | " | 0.1g. $Cr_2(SO_4)_3$ | trace |
| 21 | " | " | " | " | " | 2 |
| 22 | " | " | " | " | 0.1g. $MnSO_4$ | trace |
| 23 | " | " | " | " | " | 45 |
| 24 | " | " | " | " | 0.1g. $Ce_2(SO_4)_3$ | trace |
| 25 | " | " | " | " | " | 6 |
| 26 | " | " | " | " | 0.1g. $Th(SO_4)_2$ | trace |
| 27 | " | " | " | " | " | 15 |
| 28 | " | " | " | " | 0.1g. NaF | trace |
| 29 | " | " | " | " | " | 15 |
| 30 | " | " | NichChrome | " | 0.1g. $UO_2SO_4$ | trace |
| 31 | " | " | gauze | " | " | 100 |
| 32 | " | " | Pt | " | " | trace |
| 33 | " | " | " | " | " | 6 |
| 34 | sodium acetate | " | " | " | " | none |
| 35 | " | " | " | " | " | " |
| 36 | $Na_2CO_3$ | " | " | " | " | " |
| 37 | " | " | " | " | " | " |
| 38 | sodium acetate | " | " | " | " | " |
| 39 | 15g. $H_2SO_4$ | " | Fe | " | " | " |
| 40 | " | C | C | 2sq.dm. | " | trace |
| 41 | " | Pt | $PbO_2$ on Pb | " | " | tarry prod. |
| 42 | " | " | " | " | " | " |
| 43 | " | " | " | " | " | 57 |
| 44 | " | " | " | " | 0.1g. $MnSO_4$ | 40 |

A sample of the dye-stuff made by the above method was examined in the dye-testing laboratory of the E. I. DuPont de Nemours & Co., Lodi, N. J., and they report as follows:

*Strength:* 10-7.5 = 75 percent.

*Solubility:* 2A, same as standard.

*Shade:* trace bluer and duller.

The yield of dye-stuff in experiments other than No. 43, was determined by comparing the solution of the dye obtained, with a standard of equal concentration, in an E. H. Sargent & Co. plunger type colorimeter.

Further work is being conducted in these laboratories, on this topic, in the endeavor to increase the ultimate yield. Electrolytic oxidation of other leuco-bases is also to be investigated.

The data relating to the various experiments are given in the preceding table, the results obtained being discussed later.

From the above experimental data the following deductions may be made relative to the yield of dyestuff obtainable:

(1) No appreciable oxidation takes place in absence of a catalyst.

(2) Of the various catalysts used, uranyl sulfate gave the highest yields.

(3) Electrolysis at an elevated temperature is essential for efficient oxidation.

(4) Low concentration of the leuco-base, in the anolyte, promotes oxidation.

(5) Solvents and electrolytes, other than dilute sulfuric acid, gave negative results, even in the presence of a catalyst.

(6) The highest yield was obtained by the use of a nichrome gauze anode in a dilute sulfuric acid solution, with uranyl sulfate as a catalyst, at a temperature of 85°C. The ready solubility of the gauze in acid solution, makes its use undesirable.

(7) Oxidation with lead peroxide by the usual chemical method is carried out in the cold, while in the electrolytic method, higher temperatures are necessary.

## DISCUSSION.

ALEXANDER LOWY: This paper deals with electrolytic oxidation. There was a discussion some time ago by Dr. Thatcher in connection with the use of both anode and cathode compartments of an electrolytic cell, whereby simultaneous oxidation and reduction is carried on. We just started work at the University of Pittsburgh on another dye, *viz.*, safranine. For the preparation of this dye reduction and subsequent oxidation is required. We are carrying on research work in order to investigate whether the reduction could be accomplished in the cathode compartment, then the catholyte transferred to the anode compartment for oxidation. If we get any positive results on this method, we will report them later. Methyl violet is prepared by the oxidation of dimethylaniline by means of a long drawn out process. We are investigating the preparation of this dye by electrolytic oxidation.

F. A. LIDBURY[1]: I would like to ask whether there is any corrosion of the metal anode?

ALEXANDER LOWY: At the beginning we get a coating of lead peroxide, and that acts as a layer. We did not notice any corrosion at all. We tested the anolyte and the dye for lead and found none present.

C. J. THATCHER[2]: Did you repeat your oxidation many times with the lead anode? Because the formation of lead sulphate is very slow.

ALEXANDER LOWY: Yes, we used the same lead peroxide anode (see data) and the same electrolyte, beginning with experiment No. 14 all the way down, and there are eight duplicate experiments that have not been outlined here.

C. J. THATCHER: I would like to ask if you have tried it for reduction, or whether this double reduction and oxidation is the first time it has been tried?

ALEXANDER LOWY: The formation of this particular product is just oxidation, but in the case of safranine it will be simultaneous oxidation and reduction. This particular problem has not involved any reduction at all.

[1] Works Mgr., Oldbury Electro-Chem. Co., Niagara Falls, N. Y.
[2] New York City.

A MEMBER: So far as you know, has the electrolytic process been used for reductions?

ALEXANDER LOWY: Yes, aniline can be made on a commercial scale from nitrobenzene by electrolytic reduction, and some other products can be made directly by electrolytic reduction, as for instance, p-amidophenol, etc. In Germany aniline is made by electrolytic reduction of nitrobenzene, and a yield of 90 to 95 percent of aniline is obtained.

C. J. THATCHER: Aniline is about the easiest compound to make by electrolytic reduction of nitrobenzene. Paramidophenol is difficult as the author brought out; poisoning effects are active and are difficult to avoid. They are really catalytic; they accelerate some electrode processes more than others; I think such effects occur more frequently in reduction than in oxidation.

ALEXANDER LOWY: The reason we undertook this particular problem was because there has been comparatively little work done on electrolytic oxidation; also to see if there is any possibility of oxidizing these organic compounds by the electrolytic process in order to prepare the product that has been made by the chemical process.

A. W. BURWELL[3]: I wish to say in answer to this last statement that we have been making and have made in Cleveland, several hundred pounds of pthalic anhydride electrolytically, and in the case of hydroquinone the benzol floats from the anode to the cathode and results in hydroquinone. We use both sides of the reaction at the same time. I am not at present permitted to give any details, therefore I have prepared no paper, but in another year we will have considerable on it.

ALEXANDER LOWY: There is a concrete case of electrolytic organic process. If you make hydroquinone by the chemical process you start out with aniline, then oxidize the aniline, and then reduce the benzoquinone. The yield is far from being high. In the electrolytic process, if you can directly oxidize aniline or benzene and pass the solution from the anode compartment to the cathode compartment, I am almost sure you can compete with the chemical method, because the yields are somewhat low by the chemical method and the electrolytic method saves the chemical oxidizing and reducing agents.

[3] Consulting Chemist, Poughkeepsie, N. Y.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, President Acheson Smith in the Chair.*

# THE ELECTROLYTIC DISSOCIATION OF CYANAMIDE AND SOME OF ITS SALTS IN AQUEOUS SOLUTIONS.[1]

By Naoto Kameyama.[2]


## Abstract.

This research was carried out for the purpose of determining the degree of dissociation and the degree of hydrolysis of sodium and calcium cyanamide. With these values the dissociation constant was calculated, and the mobility of the cyanamide anion estimated. [A. D. S.]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## INTRODUCTION.

In view of the promising future of lime-nitrogen in the synthetic production of organic nitrogenous compounds, general knowledge concerning the properties, especially the electrolytic dissociation of cyanamide and its salts in aqueous solutions, is preeminently important. It is well known that cyanamide is of a very weak acidic nature, its aqueous solution not giving the acid test with the usual indicator. Bader[3] has found that it does not conduct the electric current. Grube and Krueger[4] in the course of their investigations on the polymerization of cyanamide tried to determine the primary dissociation constant of cyanamide. By means of the hydrogen electrode, they measured the hydroxyl ion concentration of solutions obtained by mixing a solution of cyanamide with caustic soda or ammonia in various proportions; from the hydroxyl ion concentrations thus found, they calculated the degree of hydrolysis and then the dissociation constant. The several cal-

[1] Manuscript received August 29, 1921. This work forms part of a paper to be published in the Journ. of College of Engineering, Tokyo Imperial University, Vol. XI., 1921.

[2] Assistant Professor of Applied Chemistry, Faculty of Engineering, Tokyo Imperial University.

[3] Z. Phys. Chem., 1890, 6, 300.

[4] Z. Phys. Chem., 1914, 86, 64.

culated values for this constant did not agree, but varied between 15-and 1.6-$10^{-12}$ and, according to the investigators, the greater value would perhaps be the more reasonable. To the author's knowledge their investigation is the only one published that has treated the present problem in a quantitative way.

In the work herein reported, the author attempted to measure the degree of dissociation as well as the degree of hydrolysis of both sodium and calcium cyanamide for the purpose of calculating the primary dissociation constant, and further to estimate the mobility of the cyanamide anion.

## DETERMINATION OF THE PRIMARY DISSOCIATION CONSTANT.

The only procedure that will give satisfactory results for a weak acid of this kind consists in first measuring the degree of hydrolysis of the alkali salt and then in calculating the hydrolysis constant and the dissociation constant.

The hydrolysis proceeds as follows:

$$Na.CN_2H + H_2O = NaOH + CN_2H_2 \qquad (1)$$

or if only the partaking ions are considered:

$$CN_2H' + H_2O = OH' + CN_2H_2 \qquad 1')$$

Let h represent the degree of the hydrolysis, and v the molecular dilution of sodium acid cyanamide, then

$$\text{Hydrolysis constant } K_h = \frac{(NaOH)\,(CN_2H_2)}{(Na\,.\,CN_2H)} = \frac{h}{1-h}\cdot\frac{1}{v}$$

$$\text{Dissociation constant } K_a = \frac{(H^{\bullet})\,CN_2H')}{(CN_2H_2)} = \frac{K_w\,\alpha_{NaCNH}{}^{*}}{K_a\,\alpha_{NaOH}{}^{*}} \qquad (2)$$

The degree of hydrolysis was determined by the measurement of conductivity of the hydrolyzed solution of sodium acid cyanamide, as:

$$\lambda_h = h\,.\,\lambda_{NaOH} + (1-h)\,.\,\lambda_o$$

$$h = \frac{\lambda_h - \lambda_o}{\lambda_{NaOH} - \lambda_o} \qquad (3)$$

* Degree of dissociation.

where $\lambda_{NaOH}$ $\lambda_h$ and $\lambda_o$ are the equivalent conductivities of caustic soda, hydrolyzed and unhydrolyzed sodium cyanamide respectively—all in the same dilution with respect to the sodium component. The last of the three was obtained by preventing hydrolysis with a large excess of free cyanamide which does not contribute to conductance in a measurable degree.

## CONDUCTIVITY MEASUREMENTS.

The solutions, the conductivities of which were to be measured, were prepared in a conductivity vessel by mixing the solution of caustic soda and that of cyanamide in various proportions. The former solution was prepared from metallic sodium. Cyanamide was prepared by eliminating calcium from calcium cyanamide by the use of oxalic acid, which in turn was prepared according to the method described in the author's previous paper.* It was purified by being dissolved in ether and then evaporating the solution. The constant of the conductivity vessel used = 0.21389 at 25° C. All of the following figures of conductivities refer to 25° C. They are the average of two or, sometimes, three determinations.

| | | A | B | C | D |
|---|---|---|---|---|---|
| v. dilution of Na component, lit./g. mol. ..... | | 9.986 | 19.97 | 39.94 | 78.88 |
| | $\lambda_{NaOH}$ | 220.33 | 223.98 | 228.44 | 233.12 |
| Mol. ratio. | | | | | |
| $H_2CN_2$/NaOH 1 | $\lambda_h$ | 91.77 | 98.72 | 105.83 | 113.80 |
| " 1.5 | | 86.65 | 91.25 | 94.45 | 97.57 |
| " 2 | | 86.01 | 90.82 | 94.13 | 97.77 |
| " 4 | $\lambda_o$ | 85.62 | 89.99 | 93.26 | 96.16 |

The great decrease in the equivalent conductivity of caustic soda by the addition of cyanamide is evidently due to the salt formation, the more conductive alkali being replaced by the less conductive salt. With an increasing amount of cyanamide, $\lambda$ becomes smaller, but the change in the last two in the above table is very small. Therefore we may take the last as $\lambda_0$, the conductivity of the unhydrolyzed salt.

* Journ. College of Engineering, Tokyo Imperial University, Vol. X. No. 8.

DEGREE OF HYDROLYSIS AND PRIMARY DISSOCIATION CONSTANT.

Inserting the values found above in equation (3), we have:

| | A | B | C | D |
|---|---|---|---|---|
| h (percent) | 4.57 | 6.52 | 9.30 | 12.88 |

The degrees of dissociation of caustic soda and of unhydrolyzed sodium cyanamide (see later) as given by ${}_v\lambda/{}_\infty\lambda$ from the author's data, taking ${}_\infty\lambda_{OH'} = 219$[5] and ${}_\infty\lambda_{Na.} = 50.9$[5], are as follows:

| | A | B | C | D |
|---|---|---|---|---|
| $\alpha NaOH$ . . . . | 81.64 percent | 82.99 percent | 84.65 percent | 96.38 percent |
| $\alpha Na.CN_2H$ . . . | 81.34 percent | 85.46 percent | 88.57 percent | 91.32 percent |
| Ratio $\frac{\alpha NaOH}{\alpha NaCN_2H}$ | 1.0040 | 0.9711 | 0.9557 | 0.9458 |

Inserting these values, and the value of h found above in the equations (2), we have:

| | A | B | C | D |
|---|---|---|---|---|
| $K_w / K_a 10^4$ | 2.196 | 2.209 | 2.282 | 2.153 |

Taking the average of these four values,

$$K_w/K_a = 2.210 \times 10^{-4} \text{ at } 25° \text{ C.},$$

and assuming $K_w = 1.2.10^{-14}$ at this temperature,

$$K_a = 5.422 \times 10^{-11} \text{ at } 25° \text{ C.}$$

This is the same order of magnitude as that of the secondary dissociation of carbonic acid ($K = 1.1 \times 10^{-11}$), or that of phenol ($13$ or $10.9 \times 10^{-11}$).

MOBILITY OF ACID CYANAMIDE ANION AT 25° C.

The equivalent conductivity of unhydrolyzed sodium acid cyanamide at infinite dilution was estimated from $\lambda_0$, found above, by means of the following well-known formula[6] for strong electrolytes:

$$\frac{I}{{}_v\lambda} = \frac{I}{{}_\infty\lambda} + k\left(\frac{{}_v\lambda}{v}\right)^{n-1} \qquad (4)$$

[5] Foerster, Elektrochemie d.waess. Lsg. 2, Auff. 92.

[6] Noyes, Electrical Conductivity of Aqueous Solutions (1907), 50.

Among various values of n applied, 1.45 was found best; this value gives:

$$_{\infty}\lambda = {}_{\infty}\lambda_{HCN'_2} + {}_{\infty}\lambda_{Na} . = 105.3 \text{ at } 25° \text{ C.}$$

As is well known,

$$_{\infty}\lambda_{Na} . = 50.9^{5} \text{ at } 25° \text{ C.}$$

therefore we have

$$_{\infty}\lambda_{CN_2H'} . = 54.4 \text{ at } 25° \text{ C.}$$

Accordingly, the conductivity of the unhydrolyzed sodium acid cyanamide and its anion are rather large. Among the various monovalent organic anions, the only one of which the conductivity is comparable with the cyanamide anion, $CN_2H'$, is that of formate, $CO_2H'$, which, according to Bredig,[7] is 54.8 at 25° C. These two anions have almost equal conductivities or mobilities, which are far greater than those of other fatty acid anions. It is interesting to note that the cyanamide anion has two nitrogen atoms in place of the two oxygen atoms in the case of the formate anion.

## DEGREE OF DISSOCIATION OF SODIUM ACID CYANAMIDE AT 25° C.

The degrees as given by $_{v}\lambda / _{\infty}\lambda$ are as follows:

| | | | | |
|---|---|---|---|---|
| Dilution, lit/mol., v. ..... | 9.986 | 19.97 | 39.94 | 78.88 |
| Dissociation (percent) ..... | 81.31 | 85.46 | 88.57 | 91.32 |

These figures refer only to the unhydrolyzed salt. They are almost equal to those of sodium formate, and very nearly equal to those of the acetate and acetylcyanamide of sodium.

## THE PRIMARY DISSOCIATION CONSTANT AT OTHER THAN 25° C.

According to Lemoult,[8] the heat of neutralization of cyanamide in solution is 3,700 cal., from which we find heat of dissociation of cyanamide at ordinary temperature = —10,000 cal., assuming the heat of neutralization of strong acid by strong base as 13,700 cal.[9]

The primary dissociation constants at temperatures other than 25° C. have been calculated, by means of the integrated reaction isochore, with the constant at 25° C. and the heat of dissociation as

[7] Z. Phys. Chem., 1894, **13**, 232.
[8] Ann. Chim. et Phys. (7), 1899, **16**, 338 ff. esp. 402
[9] Nerst, Theoretical Chemistry, Engl. Ed., 1911, 610; Landolt and Bornstein, "Tabellen," 873.

found above, under the assumption that the change of the latter is practically negligible for the temperature range here to be considered, with the following result:

| | | | | | |
|---|---|---|---|---|---|
| Temperature, °C. ..... | 0 | 25 | 50 | 80 | 100 |
| $K_a 10^{11}$ ..... | 1.154 | 5.42 | 20.1 | 75.6 | 163 |

This shows that the constant at 100° C. is about 30 times that at 25° C.

### SOLUTION OF CALCIUM ACID CYANAMIDE.

Similar to the above method, the conductivities of solutions of calcium acid cyanamide, $Ca(CN_2H)_2$, were measured, the solutions being prepared by dissolving the calculated amount of calcium oxide in the cyanamide solution.

The equivalent conductivities at 25° C. are as follows:

| | A | B | C | D |
|---|---|---|---|---|
| Dilution, lit./g. equiv..... | 10.59 | 21.9 | 42.37 | 84.75 |
| Ratio, $CN_2H_2/\frac{1}{2}Ca(OH)_2\lambda_h$ .....1.0 | 84.1 | 93.7 | 103.2 | 112.7 |
| " " .....3.3 | 82.6 | 89.8 | 94.7 | 99.9 |
| " " $\lambda_o$.....4.6 | 82.5 | 89.4 | 94.1 | 98.1 |

The indications are that hydrolysis is prevented almost entirely by the use of 4.6 mol. of cyanamide per 1 equivalent of calcium hydroxide. Therefore the value in the last series of the above table may be considered as that corresponding to the unhydrolyzed salt.

According to Noyes and Falk,[10] $_\infty\lambda_{\frac{Ca''}{2}} = 60.0$ at 25° C.; this makes $_\infty\lambda$ of $Ca(CN_2H)_2$ equal to 114.4 at 25° C. Then the degrees of dissociation of the unhydrolyzed salt as given by $_v\lambda/_\infty\lambda$ are as follows:

| A | B | C | D |
|---|---|---|---|
| 72.15 percent | 78.13 percent | 82.25 percent | 85.75 percent |

These values lie near those for

$$Mg(CO_2H)_2,^{11}\ Ca(NO_3)_2^{12}\ \text{and}\ Mg(NO_3)_2.^{12}$$

[10] Journ. Amer. Chem. Soc., 1912, 479.

[11] Walden's data (Kohlrausch's "Leibuermögen," 171, for conductivity.

[12] Noyes and Falk, Journ. Amer. Chem. Soc., 1912, 470. for conductivity data.

As in the case of the sodium salt, the degree of hydrolysis may be calculated from equation (3). In the present case, however, the value $\lambda_{\frac{Ca}{2}OH}$, in the dilution in question, is not comprehensible owing to the limited solubility of calcium hydroxide. We may assign values which the solution would have if it were possible to exist in such concentrations, not being restricted by the solubility. Now the portion of the curve log. v vs. $\lambda$, in the dilution in question, is nearly a straight line for $Ba(OH)_2$ and $Sr(OH)_2$. Therefore, we may extrapolate the same curve of $Ca(OH)_2$,[13] without introducing any serious error into the range required. Of course the values thus found are only approximate, but they enable us to orientate the values of h by equation (3), as indicated below. Comparison is made with the values expected from the dissociation constant previously found.

| | A | B | C | D |
|---|---|---|---|---|
| $\lambda_{\frac{Ca}{2}OH}$ assumed ..... | 176.1 | 186.5 | 196.8 | 207.2 |
| h found (percent) ..... | 1.7 | 4.4 | 8.9 | 13.4 |
| h expected ..... | 5.0 | 7.1 | 9.9 | 13.8 |

In view of the nature of the estimation, the results, with the exception of the first, may be said to be satisfactory.

## SUMMARY.

Sodium acid cyanamide in aqueous solutions is hydrolyzed (at 25° C.) to the extent of 4.5 to 12.9 percent in the dilutions of 10 to 80 lit./g. mol., respectively. If this hydrolysis is prevented by an excess of cyanamide, dissociation occurs to almost the same extent as in the case of sodium formate. Under similar conditions unhydrolyzed calcium acid cyanamide dissociates to the same extent as magnesium formate or calcium nitrate.

The primary dissociation constant of cyanamide, as an acid, at

[13] Ostwald, J. Prak. Chem., 1886, *33*, 352. Recalculated from the original, $\mu$, the molecular conductivity, = 406.0, 426.8, 446.1, 455.0 or v = 64,128,256,512. Values cited in Kohlrausch's "Leitvermoegen," p. 167, seem to contain some misprints.

25° C., was found to be $5.42.10^{-11}$; the values at other temperatures were calculated from the heat of dissociation.

The conductivity of the cyanamide anion has been found to be 54.4 at 25° C., a value nearly equal to that of the formate anion, which, according to Bredig, is 54.8.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, Vice-President Schluederberg in the Chair.*

# ELECTROLYTIC PRODUCTION OF SODIUM PERBORATE.[1]

By Peder Chr. Alsgaard.[2]

Abstract.

A detailed account of the research work by Arndt and by Valeur, in producing sodium perborate electrolytically, is given. The author presents the results of his preliminary experiments and their application to larger scale production. [A. D. S.]

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The perborates, and principally the sodium perborate, have been used extensively for a long time in the industry, chiefly as bleaching agents for all kinds of more delicate articles, such as silk, feathers, ivory, animal fibres, wool, etc. They are used to a great extent in connection with washing powders, and, due to the presence of soap powders, soda ash, etc., they produce a bleaching effect in addition to the cleansing one. As a disinfectant and antiseptic they find use in medicine.

The properties of the solutions of the perborates correspond exactly to those of hydrogen peroxide, oxygen being split off readily in both cases. Thus sodium perborate gives off one atom of oxygen forming sodium metaborate:

$$NaBO_3 \rightarrow NaBO_2 + O$$

just in the same way as hydrogen peroxide gives off oxygen forming water:

$$H_2O_2 \rightarrow H_2O + O$$

This analogy is shown further by the fact that each is converted very readily into the other. When sodium perborate is treated with a dilute acid, hydrogen peroxide results. If the latter is

[1] Manuscript received August 12, 1921.

[2] Graduate Student, Cornell University, Ithaca, N. Y.

added to a solution of metaborate—as borax and sodium hydroxide—the reverse reaction takes place, and the perborate is regenerated. Because of these properties, the sodium perborate may always replace the hydrogen peroxide chemically. Since it crystallizes readily, and is then very stable and can be kept indefinitely at the ordinary temperature, it affords a very convenient substitute for hydrogen peroxide. The content of active oxygen in sodium perborate is 10.4 percent, according to the formula $NaBO_3.4H_2O$, while the common 3 percent hydrogen peroxide contains only 1.4 percent of active oxygen and is very unstable.

In the previous processes for the manufacture of sodium perborate, hydrogen peroxide was usually used as the oxidizing agent and was simply poured into a solution of borax and sodium hydroxide or soda ash, whereupon the perborate crystallized out in large crystals. Instead of hydrogen peroxide other oxidizing agents may be used, such as percarbonates or sodium peroxide. From the latter, it is also possible to obtain a compound called "Perborax," $Na_2B_4O_8$, having practically the same properties as sodium peroxide. All these processes, however, are rather complicated, as they imply the intermediate preparation of an oxidizing agent, for example, hydrogen peroxide, the production of which is rather difficult and expensive. Much work was therefore done by several investigators, in an endeavor to find a more direct and economic process for the manufacture of sodium perborate by the electrolysis of borax solutions. The difficulties, however, involved in the solution of this problem, seemed for a long time to be as great as those involved in the electrolytic production of hydrogen peroxide.

Upon the request of Die Chemische Fabrik Grünau, Berlin, Professor Kurt Arndt started some research work[3] on this problem, and in 1912 he happened to observe that sodium perborate was formed when electrolyzing a solution of borax containing sodium carbonate.

By the electrolysis of a solution containing sodium carbonate and borax, sodium percarbonate is probably formed as an intermediate, which reacts instantaneously with borax forming perborate. By this process it is possible to produce sodium perborate

[3] Cf. Zeitschrift für Elektrochemie, 1916, 22, 63.

directly, doing away with the peroxides of hydrogen and sodium. The importance of this invention is obvious.

Some years ago Trygne Valeur did some research work at the Institute of Technology of Norway, in connection with the electrolytic production of sodium perborate. At that time he did not know anything of the work of Kurt Arndt, and the results obtained were absolutely misleading. In spite of variation of working conditions, and use of different electrolytes, the quantities of sodium perborate obtained were very small. What made the problem look rather hopeless was further the fact that on electrolyzing a solution containing some sodium perborate, this was decomposed, no matter whether a diaphragm was used or not. It thus appeared that on electrolyzing a solution of sodium perborate, it is decomposed anodically as well as cathodically. After becoming aware of the patents taken out by Kurt Arndt, Valeur resumed his research work, and as his results were of great value for the subsequent development of a technical process for the electrolytic production of sodium perborate, they are first dealt with at some length[4].

Since sodium perborate is more unstable at high temperatures, it is most likely that a better current efficiency will result at lower temperatures. On the other hand, the solubility of borax is very small in cold water, and as it may be assumed that the current efficiency increases with increasing concentration of borax in the electrolyte, the first experiments were carried out with a solution of borax and sodium hydroxide. On account of the greater solubility of the metaborate, such a solution can be made rather concentrated, even at a low temperature.

In order to increase the current efficiency a diaphragm was first used. As this causes the alkalinity of the anodic solution to decrease, the borax has a tendency to crystallize if no precautions are taken. For this reason, from the beginning of the electrolysis, there was added an excess of sodium hydroxide, and the electrolysis continued until the borax began to crystallize out. From the results thus obtained, we gained an idea of the influence of alkalinity on the formation of the sodium perborate. It now appeared that the concentration of the sodium perborate always increased during the electrolysis, up to the point where

[4] Cf. Tidsskrift for Kemi, Farmaci og Terapis, Kristiania, 1916, No. 17, 18.

the crystallization of the borax sets in. From that moment it begins to decrease, although very slowly. It was further found that this maximum concentration of sodium perborate, within a wide range, was nearly independent of the quantity of sodium hydroxide originally added, and hence, independent of the time from the start of the experiment until the beginning of the crystallization of the borax. This indicates that under the prevailing conditions the maximum concentration found is the largest obtainable at all. Since the sodium perborate is not only produced, but also decomposed at the anode, it seems very probable that there must be a concentration, at which the formation and the decomposition of the perborate counterbalance each other.

TABLE I.

| No. | Contents per 100 cc. of Electrolyte | Voltage across cell | Temperature | Maximum Concentration |
|---|---|---|---|---|
| 1 | 4 g. $Na_2CO_3$ + 8g. NaOH+ 17 g. $Na_2B_4O_7 . 10H_2O$ | 6.0—7.9 | 9°—13°C | 2.3 |
| 2 | 8 g. $Na_2CO_3$ + 8g. NaOH+ 17 g. $Na_2B_4O_7 . 10H_2O$ | 6.2—7.7 | 9°—16°C | 3.9 |
| 3 | 12 g. $Na_2CO_3$ + 8g. NaOH+ 17 g. $Na_2B_4O_7 . 10H_2O$ | 6.4—7.4 | 9°—14°C | 5.0 |
| 4 | 16 g. $Na_2CO_3$ + 8g. NaOH+ 17 g. $Na_2B_4O_7 . 10H_2O$ | 6.5—7.7 | 9°—14°C | 5.7 |

At first some experiments were carried out to determine the influence of the sodium carbonate on the production of the sodium perborate. The diaphragm used was a porous cylindrical clay cell, containing 85 cc. of the anodic solution. The cell was placed in a beaker containing *N/1* NaOH as cathodic solution. The anode was a platinum sheet with a total surface of 6.4 sq. cm. The current was 1.6 amperes and the anodic current density thus 25 amp./sq. dm. The cathode consisted of an iron plate surrounding the diaphragm cell. In order to keep down the temperature, the beaker was placed in ice water. The reagents used in these experiments were very pure, as impurities proved harmful. The sodium perborate produced was titrated in the usual way with *N/10* $KMnO_4$ in an acid solution (Table I).

The figures for the maximum concentration refer to the amount of *N/10* $KMnO_4$ (in cc.) used for the titration of 1 cc. of electrolyte. The maximum concentration was reached after 6-8 hours of electrolysis. It appears that the production of sodium perborate is increased essentially by increasing the concentration of sodium carbonate in the electrolyte, which is only what might have been expected beforehand. In experiment No. 4 the solution is decidedly supersaturated with respect to the sodium carbonate; but no salt crystallized during the electrolysis, nor was there any precipitation of sodium perborate in any of the experiments. If, instead of sodium carbonate alone, a mixture of sodium and potassium carbonate is used in the electrolyte, a still higher maximum concentration of sodium perborate may be obtained. Some experiments were then carried out with elec-

TABLE II.

| No. | Contents per 100 cc. of Electrolyte | Voltage across cell | Temperature | Maximum Concentration |
|---|---|---|---|---|
| 5 | 8 g. $Na_2CO_3$ + 8 g. NaOH+ 17 g. Borax+3 cc. water-glass | 7.4—8.1 | 9°—14°C | 5.25 |
| 6 | 12 g. $Na_2CO_3$ + 8 g. NaOH+ 17 g. Borax+3 cc. water-glass | 6.6—7.8 | 9°—14°C | 6.65 |
| 7 | As in experiment 6 | 7.1—7.5 | 9°—14°C | 7.05 |

trolytes corresponding to those in Table I, but with an addition of small amounts of different substances. Thus sodium fluoride was tried, which raises the overvoltage; also sodium phosphate, which is stated to stabilize perborate solutions, and many others. In most cases the addition had practically no effect upon the formation of the perborate, and in some they were detrimental. Sodium silicate—water-glass—however, proved to be favorable, as is shown by the following three experiments, Table II.

Except for the content of water-glass, the working conditions of these experiments were the same as in the experiments Nos. 2 and 3 (Table I).

In all these experiments a layer of silica was formed on the anode. This layer, however, became visible only at the end of the experiment. When electrolyzing a solution containing only

water-glass, practically no sodium perborate was formed. There is therefore a marked difference between sodium carbonate and water-glass, as to their effect upon the formation of perborate. This difference is also shown by the fact that the effect of the water-glass, as contrasted with the sodium carbonate is independent of the quantity added within a wide range. In all these experiments platinum was used as an anode. It would, however, be of great interest, if the platinum could be replaced by a cheaper material.

TABLE III.

| No. | Contents per 100 cc. of Electrolyte | Current Density amp./sq. dm. | Votage across cell | Temperature C | Maximum Concentration |
|---|---|---|---|---|---|
| 8 | 12 g. sodium carbonate 8 g. NaOH + 17 g. borax | 16 | 6.0—6.7 | 8°—12° | 3.0 |
| 3 | 12 g. sodium carbonate 8 g. NaOH + 17 g. borax | 25 | 6.4—7.4 | 9°—14° | 5.0 |
| 9 | 12 g. sodium carbonate 8 g. NaOH + 17 g. borax | 35 | 7.4—8.0 | 10°—14° | 4.0 |
| 10 | 12 g. sodium carbonate 8 g. NaOH + 17 g. borax | 50 | 7.2—8.6 | 9°—16° | 3.8 |
| 11 | 12 g. $Na_2CO_3$+8 g. NaOH+ 17 g. borax + 3 cc. water-glass | 16 | 7.0—7.5 | 10°—14° | 5.4 |
| 12 | 12 g. $Na_2CO_3$+8 g. NaOH+ 17 g. borax + 3 cc. water-glass | 25 | 6.4—8.0 | 9°—15° | 6.5 |
| 13 | 12 g. $Na_2CO_3$+8 g. NaOH+ 17 g. borax + 3 cc. water-glass | 35 | 7.5—8.5 | 10°—14° | 6.6 |
| 14 | 12 g. $Na_2CO_3$+8 g. NaOH+ 17 g. borax + 3 cc. water-glass | 50 | 8.2—9.2 | 9°—16° | 6.1 |

Experiments were therefore carried out with lead, nickel, iron, and graphite; but these metals all proved unsuitable. In some cases—lead and nickel—some perborate was formed; but the amounts were too small to make them available. By the use of an anode of nickel, the maximum concentration obtained corresponded to the amount of 0.5 cc. of $N/10$ $KMnO_4$ used per 1 cc. of the electrolyte.

The next problem was to determine the effect of the current density upon the maximum concentration of sodium perborate.

From the previous experiments it follows that the concentration of the sodium carbonate should be as high as possible, and for that reason, the electrolyte in all cases was practically saturated with sodium carbonate. The working conditions were exactly as in the previous experiments. The current was always 1.6 amperes and consequently the size of the anode had to be varied in order to get a variation in the current density. The results of these experiments are tabulated in Table III. From this it will be seen that the most favorable current density varies from 25-35 amp./sq. dm. When the electrolyte contains water-glass, this favorable current density is apparently somewhat higher than in the cases where no water-glass is used. These experiments also show the favorable influence of the water-glass on the maximum concentration of the sodium perborate.

TABLE IV.

| No. | Contents per 100 cc. of Electrolyte | Voltage across cell | Temperature | Maximum Concentration |
|---|---|---|---|---|
| 15 | 8 g. $Na_2CO_3$ + 8 g. NaOH + 7 g. borax + 3 cc. water-glass | about 10.0 | 5°—10°C | 4.7 |
| 16 | 12 g. $Na_2CO_3$ + 8 g. NaOH + 17 g. borax + 3 cc. water-glass | 6.4—7.8 | 10°—14°C | 5.45 |
| 17 | 16 g. $Na_2CO_3$ + 8 g. NaOH + 17 g. borax + 3 cc. water-glass | 6.9—7.5 | 16°—22°C | 4.5 |

Besides the current density, there is another factor that might be of importance to the current efficiency, namely, the temperature. When determining the temperature most favorable to the electrolysis, it must be borne in mind that the solubility of the sodium carbonate will vary at the different temperatures. When varying the temperature, it is therefore necessary also to vary the composition of the electrolyte, and to take care that the electrolyte is always practically saturated with sodium carbonate. In this way the most favorable temperature was found to be about 10°-12° C., which is shown by the following three experiments, Table IV.

The experimental conditions were as before—current density 25 amp./sq. dm., the only difference being that the borax had

not been recrystallized, and therefore a decrease in the current efficiency resulted.

In spite of the fact that the concentration of the sodium perborate in many of the solutions was rather high, it never crystallized, even when the solution was cooled down to 0°C. This is rather peculiar, as the solubility of sodium perborate in water is rather low. In order to get a more general idea as to the condition of solubility, some experiments were made with very strong solutions of sodium perborate, prepared by means of hydrogen peroxide. The solutions were inoculated with crystals of sodium perborate and allowed to stand at 0°C. for crystallization. By

TABLE V.

| No. | Contents per 100 cc. of electrolyte | Voltage across cell | Temperature | Maximum Concentration |
|---|---|---|---|---|
| 9 | 12 g. $Na_2CO_3$ + 8 g. NaOH + 17 g. borax | 7.4—8.0 | 10°—14°C | 4.0 |
| 13 | 12 g. $Na_2CO_3$ + 8 g. NaOH + 17 g. borax + 3 cc. water-glass | 7.5—8.5 | 10°—14°C | 6.6 |
| 18 | 12 g. $Na_2CO_3$ + 5.5 g. NaOH + 12 g. borax | 8.0—8.3 | 11°—14°C | 4.2 |
| 19 | 12 g. $Na_2CO_3$ + 5.5 g. NaOH + 12 g. borax + 3 cc. water-glass | 7.2—7.7 | 10°—13°C | 5.5 |
| 20 | 12 g. $Na_2CO_3$ + 4.5 g. NaOH + 8 g. borax | 7.4—7.9 | 11°—14°C | 4.1 |
| 21 | 12 g. $Na_2CO_3$ + 4.5 g. NaOH + 8 g. borax + 3 cc. water-glass | 7.5—8.0 | 11°—14°C | 5.2 |

making continuous analyses of the solution, the rate of crystallization could be followed, and the solubility determined in the different cases. First it proved that the sodium perborate has a very marked tendency to form supersaturated solutions. Usually crystallization does not take place unless the solution is inoculated, and, in most cases, several days were required to bring the crystallization to an end, and to get a constant amount of sodium perborate in solution. Then it proved that sodium metaborate and sodium hydroxide increase the solubility of sodium perborate, while an addition of sodium carbonate causes some decrease in the solubility. It may be noted that it proved impos-

sible to induce the sodium perborate to crystallize at 0°C. from a solution containing per 100 cc., 33 g. of borax, 12 g. of NaOH, and 20 cc. of about 10 percent $H_2O_2$, although the equivalent of *N*/10 $KMnO_4$ per cc. of the solution was 12-13 cc. In pure water, however, the solubility was much less, the amount of *N/10* $KMnO_4$ used per cc. being only 1.2 cc. The reason for these solubility relations is most probably the formation of some complex or double salt. These changes in solubility are very important when making sodium perborate on a technical scale. The only thing to do in this case seems to be to use solutions containing less metaborate. In order to illustrate the state of things, when decreasing amounts of metaborate are in solution, the results of some experiments are given in Table V. The working conditions were as described before and the current density was 35 amp./sq. dm.

As mentioned before, it was impossible to induce crystallization of the sodium perborate in the experiments 9 and 13. In experiments 18 and 19, however, after cooling down to 0°C. and filtering off the sodium carbonate which crystallized out, small quantities of sodium perborate were induced to crystallize by inoculation with sodium perborate crystals, and in the experiments 20 and 21, after inoculation of the solution, the sodium perborate crystallized at the temperature used in the electrolysis (12-13° C). The favorable effect of the water-glass is also observed in these experiments, but it is also seen that the influence decreases with the concentration of the borate in the electrolyte, and to such an extent that the maximum concentration without water-glass is practically independent of the concentration of the borate, while the decrease is very marked where water-glass is present in the solution.

As soon as it is possible to prepare solutions saturated or super-saturated with respect to sodium perborate, the most important question is no longer the maximum concentration, but the current efficiency at that concentration of sodium perborate where the solution is saturated.

When, in the experiments 20 and 21, the amounts of sodium hydroxide are varied, the time required for attaining the maximum concentration varies also, as does the current efficiency. The highest current efficiency obtained in this way at

the concentration of the saturated solution, was 35 percent with, and 30 percent without, water-glass in the electrolyte. At the temperature used (12°-13° C.) the concentration of the saturated solution corresponded to an amount of about 2.7 cc. of *N/10* $KMnO_4$ used per cc. of the electrolyte.

This is, however, still rather high and it proved more favorable to work with solutions containing no sodium hydroxide at all, hence no metaborate. The maximum concentration certainly decreases appreciably when doing so, as the content of borate in the solution becomes rather small; but at the same time the solubility of the sodium perborate decreases to such a degree that the current efficiency at that concentration of the saturated solution increases considerably. A further advantage is the possibility of doing away with the diaphragm. This is certainly

TABLE VI.

*Experiment 22.*

| Amp. Hrs. from Start of the Experiment | No. of cc. *N/10* $KMnO_4$ | Current Efficiency in Percent |
|---|---|---|
| 0 | 0 | 49.5 |
| 0.5 | 1.1 | 33.8 |
| 1.0 | 1.85 | 29.2 |
| 1.5 | 2.5 | .... |

practicable also in the previous experiments, where sodium hydroxide is used. The losses in current efficiency, due to cathodic reduction of the perborate, increase, however, rather noticeably with increasing concentration of the perborate. When therefore no diaphragm is used, the decrease in current efficiency is much greater, when the electrolyte contains sodium hydroxide, as compared with the cases where no sodium hydroxide is employed, and the concentration of sodium perborate therefore is much less. The concentration of such a solution, when saturated, corresponds to the equivalent of only 0.9-1 cc. of *N/10* $KMnO_4$ per cc. of the solution (cf. exp. No. 22). The variation of the current efficiency in relation to the concentration of perborate may be seen from Table VI. The solution employed contained per 100 cc., 12 g. of $Na_2CO_3$, 4.5 g. of crystallized

borax, and 0.2 g. of sodium bichromate. The cathode consisted of two zigzag bent nickel wires, one on each side of the anode, of 1.5 mm. diameter, and an effective length of 205 mm. The surface was accordingly about 9.6 sq. cm. The current was 1.6 amperes; the current density thus about 17 amp./sq. dm.; the anodic current density 35 amp./sq. dm.; the volume of the solution 85 cc.; the temperature 11-13° C.; and the voltage across the cell about 6.5 volts.

As previously mentioned, it is also practicable, instead of sodium carbonate alone, to employ a mixture of sodium and potassium carbonate in the electrolyte. This makes it possible to increase the total amount of carbonate in the solution, which, in turn increases the maximum concentration of the sodium perborate

TABLE VII.

*Experiment 23.*

| Amp. Hrs. from Start of the Experiment | No. of cc. *N/10* $KMnO_4$ | Current Efficiency in Percent |
|---|---|---|
| 0 | 0 | 54. |
| 0.5 | 1.2 | 40.3 |
| 1.0 | 2.45 | 30.9 |
| 1.5 | 3.0 | .... |

as well as the current efficiency. The addition of potassium carbonate, however, increases simultaneously the solubility of the sodium perborate, and as we are here concerned chiefly with the current efficiency at the concentration of a saturated solution, this effect to some extent counterbalances the increase in current efficiency. When the amount of potassium carbonate is not too large, this increase in solubility is relatively small. The best results were obtained with a solution containing per 100 cc., 10 g. of sodium carbonate, 7 g. of potassium carbonate, 4.5 g. of borax and 0.2 g. bichromate, cf. Table VII. The concentration of the saturated solution in this case corresponded to an amount of 1.1 cc. *N/10* $KMnO_4$ per 1 cc. of electrolyte. The temperature was maintained at 10°-13° C., and the voltage was about 6 volts. For the remainder of the experiment, the working

conditions were the same as those employed in experiment No. 22. In this experiment an addition of water-glass also proved favorable, when the amount was not too large. In Table VIII are given the results of an experiment which differs from the above experiment only in so far as the electrolyte contained three drops of water-glass per 100 cc. When sodium perborate is to be manufactured on a technical scale, the most ideal condition would be the continuous crystallization of the sodium perborate during the electrolysis, and the simultaneous addition of the raw materials as they are consumed in the process. In order to have the sodium perborate crystallize out without the concentration rising too high above the concentration of the saturated solution, the slow crystallization of the salt makes it necessary to use rather large electrolyzing cells and a relatively small current.

TABLE VIII.

*Experiment 24.*

| Amp. Hrs. from Start of the Experiment | No. of cc. *N/10* $KMnO_4$ | Current Efficiency in Percent |
|---|---|---|
| 0 | 0 | 56.4 |
| 0.5 | 1.5 | 45.0 |
| 1.0 | 2.3 | 30.1 |
| 1.5 | 3.1 | .... |

In the following are given two experiments, carried out in a relatively large electrolytic cell, with a lower surface of 660 sq. cm., and containing 2.5 liters of electrolyte.

The electrolysis was continued for a period of 40 hours. When the concentration of the saturated solution was reached, the solution was inoculated with crystals of sodium perborate. Borax and sodium carbonate were added as they were consumed in the process. In the first experiment using no water-glass—after crystallization had started and equilibrium was attained, the concentration remained between 1.8 and 1.9 cc. of *N/10* $KMnO_4$ per cc. of electrolyte. The sodium perborate, which crystallized out during the experiment, was carefully washed, dried, weighed and analyzed. The current efficiency was calculated to be 31.8 percent.

In the other experiment, using 2 cc. of water-glass per liter of the electrolyte, equilibrium was established at an amount of 2-2.1 cc. of *N/10* $KMnO_4$ per cc. of electrolyte, and the current efficiency amounted to 37.5 percent. As the concentration of the saturated solution corresponds to the amount of about 1.1 cc. of *N/10* $KMnO_4$ per cc. of electrolyte, there is no doubt that the current efficiency can be improved considerably by using still larger electrolytic cells, in which case the equilibrium is established at a lower concentration of perborate. These experiments, carried out by Valeur cleared up the process for the electrolytic production of sodium perborate in a large measure, and threw light upon the most important factors governing the process. For the technical and commercial utiliza-

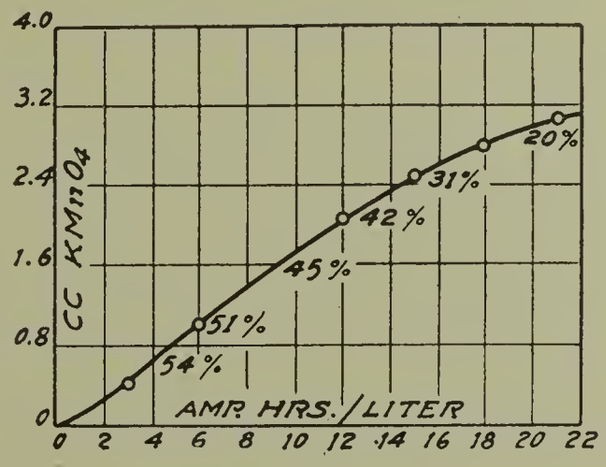


FIG. 1.

tion of the process, further important problems had to be solved, and the writer therefore, some years later, while in the employment of O. Collett & Co., started some research work in order to develop a technical process for the electrolytic production of sodium perborate. The process was in operation in Germany during the war, and plans were considered to extend the work on a very large scale.

The first experiments were practically a repetition of the experiments already carried out by Valeur, but on a somewhat larger scale. The external cooling with ice water, is of course out of the question in a technical process. The solution was therefore cooled by running cold water through the cathode, which for this purpose consisted of a pipe of copper, suitably shaped, and coated with a layer of tin or nickel. The results

obtained were practically the same as those found by Valeur. It will therefore be sufficient to refer to only one of these experiments, the results of which are shown graphically in Fig. 1. As abscissa is used the number of ampere hours per liter of the electrolyte, and as ordinate the amount of *N/10* $KMnO_4$ used per cc. of the electrolyte, 1 cc. of *N/10* $KMnO_4$ corresponding to *7.7* g. of perborate per liter of the electrolyte. The current was 6 amperes and the voltage across the cell about 6 volts. The volume of the electrolyte was 400 cc. and the temperature was kept at 9°-10° C. The electrolyte had the following composition per liter:

100 g. of $Na_2CO_3$
75 g. of $K_2CO_3$
45 g. of borax
2 g. of potassium chromate

It is seen from the curve that the current efficiency falls off as the concentration of the sodium perborate increases, and on extrapolation becomes zero. By further electrolysis the concentration of the perborate remains constant, and equal amounts of perborate are formed and decomposed. The solutions of perborate obtained, however, did not appear to be stable. When allowed to stand, the content of perborate gradually decreased. The rate of decomposition varied to some extent, but it was always noticeable in spite of the use of very pure reagents. This decomposition is inevitable, as it had been stated by Valeur that great surfaces and volumes, as compared with the load current employed, were necessary in order to cut down the concentration of the perborate and to increase the current efficiency. On account of the spontaneous decomposition of the perborate, the beneficial effect of a greater volume is of course limited, as the decomposition is proportional to the volume of the electrolyte employed. The decomposition of the sodium perborate is, as in the case of a solution of hydrogen peroxide, principally effected by the catalytic action of impurities present in the solution. It was impossible to prepare a solution which was absolutely stable, even at very low temperatures. The decomposition proved chiefly to be due to iron, which is rather peculiar, as iron is generally supposed to be insoluble in sodium carbonate. Efforts were now made to purify the raw materials. The crystallized high-

grade commercial borax (99.5 percent $Na_2B_4O_7.10H_2O$) may be used directly. The commercial soda ash, however, with 98-99 percent $Na_2CO_3$, has to be purified, as it always contains traces of iron. The content of sodium chloride is unimportant, as a concentration of 5 g. of NaCl per liter of the electrolyte does not affect the current efficiency at all. An attempt was made to precipitate and remove the iron from the solution of sodium carbonate by boiling, by addition of several substances, colloids, alumina, ferric oxide, etc.; but all in vain. The only way left was to purify the sodium carbonate by crystallization. From the equation for the formation of sodium perborate from sodium carbonate and borax: $Na_2B_4O_7 + Na_2CO_3 + 4O \rightarrow 4NaBO_3 + CO_2$, it is noticed that $CO_2$ is set free, and that the materials actually consumed are borax and sodium hydroxide. In order to maintain the initial and favorable concentration of borax and sodium hydroxide, these substances must be added to the electrolyte during the process of the electrolysis.

The employment of sodium hydroxide involves another problem, as it is very difficult to obtain this material of the purity required for the perborate electrolysis. It may be obtained from pure sodium carbonate by caustification with pure lime, or sodium carbonate may be used instead of sodium hydroxide, and the $CO_2$ formed by the electrolysis removed by treatment of the electrolyte with pure lime. However, either one of these methods is rather expensive, and not very satisfactory. A more favorable method was the caustification of the electrolyte by means of electrolysis. The electrolyte, which in this case was made purposely rich in sodium bicarbonate, was fed to the cathodic compartment of an electrolytic cell, canvas being used as a diaphragm, and electrolyzed until the greater part of the bicarbonate and carbonate of sodium was converted into sodium hydroxide. This process worked very satisfactorily; but as it requires special electrolytic cells, it makes the process more complicated.

Further experiments were therefore carried out in order to find another method for the removal of the excess of carbon dioxide. It had been observed that the carbon dioxide is partly liberated at the anode and thus removed from the electrolyte by the primary electrolytic process. As this fact may be used

for the removal of the carbon dioxide, set free by the formation of sodium perborate, some experiments were carried out in order to determine under what conditions this evolution of carbon dioxide takes place. The method which suggests itself, is to carry out the electrolysis, in such a way that the absorption of the liberated carbon dioxide is cut down to such an extent that the quantity set free corresponds to the consumption of sodium carbonate for the formation of perborate. This proved to be possible by using as an electrolyte a solution containing a large amount of sodium bicarbonate compared with the total amount of carbonate present, and by lessening the immersion of the anode in the electrolyte. It also proved favorable to work with electrolytes containing no or only small amounts of potassium carbonate. The elimination of the potassium carbonate is also desirable from the point of view of regeneration of the substances dissolved in the electrolyte. As the electrolysis proceeds, and new raw materials are added to the system, impurities gradually accumulate in the electrolyte, and the decomposing influence on the perborate becomes more marked. From time to time it is therefore necessary to replace the electrolyte partially by fresh solution.

The regeneration of the sodium carbonate and the borax from the old electrolyte does not offer any difficulties, as this is easily done by evaporation and crystallization. The regeneration of the potassium carbonate, however, and further, the purification of the commercial potassium carbonate involve several difficulties. For these reasons it would be a great advantage to use an electrolyte containing borax and sodium carbonate only, and no potassium carbonate at all. The current efficiency certainly would diminish in this case, but at the same time the lesser solubility of the perborate in the electrolyte produces better crystallization. Experiments along this line were made in connection with the next problem to be solved, namely, the crystallization of the sodium perborate from the electrolyte.

From the current efficiency curve it is noticed that the lower the concentration of the perborate in the electrolyte, the higher the current efficiency. In order to keep the concentration of the perborate low, Valeur in his last experiments used a very large lower surface as compared with the current used, and still the

concentration remained at a value corresponding to the amount of 2 cc. of *N/10* $KMnO_4$ used per cc. of the electrolyte. If the same relative area were to be used, when working on an industrial scale (one ton per day) this would mean a surface of about an acre. This is of course impossible. At the same time this involves the use of large volumes of electrolyte per ampere, which is unfortunate, because of the spontaneous decomposition of the perborate. The solution of the problem offered several difficulties, which at last were overcome, and it proved possible to reduce the volume of the electrolyte substantially. In one of these experiments 1.8 liters of electrolyte were electrolyzed with 6 amperes at a temperature of 10° C. The solution had the following composition per liter:

45 g. of borax
130 g. of sodium carbonate
45 g. of sodium bicarbonate
2 g. of potassium bichromate
2 g. of water-glass

Potassium carbonate was not used. When equilibrium was established the concentration of the perborate in solution corresponded to an amount of about 1.5 cc. of *N/10* $KMnO_4$ used per cc. of the electrolyte. The current efficiency, with reference to the washed, dried, and analyzed salt, amounted to about 40 percent.

When the research work on this preliminary smaller scale, had led to satisfactory results, and the process had been put in a shape suited for development, experiments were started on a large scale, to determine what modification of the apparatus and process was necessary; to determine, for instance, what form and dimensions of the electrodes were to be used on an industrial scale. The results from these experiments confirmed entirely the results obtained in the previous experiments, and also furnished the facts and figures necessary for the technical design of the process and the calculation of the costs of production.

As to the latter, these of course depend to some extent on the local conditions; but some figures may be stated, which give an idea of the production costs. The outstanding items are the

cost of raw materials, power and labor. The raw materials required per ton of perborate are:

| | |
|---|---|
| Borax | 700 kg. |
| Soda ash, | 200 kg. |

Assuming a production of one ton of sodium perborate per day, and 330 days of operation a year, the electric power required for the electrolysis will be:

| | Horse-power |
|---|---|
| Calculated as direct current | 315 |
| Mechanical power, power for cooling plant | 130 |
| Total power, say | 450 |

Number of laborers, about 10.

In case the perborate electrolysis is operated in connection with another electrolysis, this figure is reduced considerably. The amount of platinum required for this production is about 7 kg.

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## DISCUSSION

Jos. W. Richards[1]: About a month ago I was with one of our members, Mr. Hudson, and he has worked out an electrolytic process for making sodium borate. At the next meeting of the society we may have a paper from him on his method of producing it. He showed me some of his product.

P. C. Alsgaard: We had some trouble with iron and felt that it was due to the presence of a cyanide, but you can get pure sodium carbonate by crystallization if you stir the solution.

Jos. W. Richards: Did you say that the addition of cyanide prevented the iron from decomposing perborate?

Mr. Alsgaard: That is what the chemists found.

[1] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, Vice-President Schluederberg in the Chair.*

# THE ELECTROLYTIC OXIDATION OF HYDROCHLORIC ACID TO PERCHLORIC ACID.[1]

By H. M. Goodwin[2] and E. C. Walker, 3rd.[3]

Abstract.

An investigation of the best conditions under which hydrochloric acid may be electrolytically oxidized to perchloric acid. Data are given showing the effect of concentration of acid, current density, duration of electrolysis, and temperature on the yield of perchloric acid. A cell is then described in which the process has been carried out successfully on a scale to yield 800 grams of 60 percent acid per day of twenty-four hours.

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The purpose of the following investigation was to determine the best conditions under which hydrochloric acid could be electrolytically oxidized to perchloric acid, and to devise a cell for carrying out the process on a practical scale. That perchloric acid can be formed by the electrolysis of hydrochloric acid has long been known, the fact having been noted by Count Stadion[4] in 1816. In 1898 Haber[5] investigated the electrolysis of hydrochloric acid solutions and stated that when dilute solutions are electrolyzed, small amounts of perchloric acid are formed.

Up to the time this investigation was undertaken in 1916 perchloric acid was made by one of the following methods:

1. By heating a concentrated solution of chloric acid. As pure chloric acid is not readily prepared and the yield of perchloric acid is low this method is of little practical value.[6]

[1] Manuscript received, September 15, 1921.

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Thesis presented in partial fulfillment of requirements for the Degree of Doctor of Engineering, Mass. Inst. Technology. Grateful acknowledgment is made to Dr. A. A. Noyes for many helpful suggestions received during the progress of the work.

[4] Stadion, Gilberto, Ann. **52**, 197 and 339. See also Lieb. Ann. **56**, 281; Ann. de chine et de phys. (3), 7, 298.

[5] Haber, Zeit. für anorg. chem., **1898**, **16**, 225.

[6] Millon, Ann. de chine et de phys. (3), 7, 310; Penny, Lieb. Ann. **37**, 203.

2. By the action of fluosilicic acid on potassium perchlorate and subsequent distillation of the filtrate of dilute perchloric acid. This method is obviously difficult and of theoretical interest only.[7]

3. By the action of sulfuric acid on barium perchlorate with subsequent concentration and distillation. The chief objection is that the barium salt is expensive.[8]

4. By steam distillation under reduced pressure of a mixture of potassium perchlorate and sulfuric acid. A good yield is claimed by this method.[9]

5. By the action of concentrated hydrochloric acid on sodium perchlorate and concentration of the filtrate until excess of hydrochloric acid is driven off.[10] Mathers[11] states that this method yields 95 percent of the theoretical acid, and with cheap sodium perchlorate would seem to be the best method thus far proposed.

6. By the action of aqua regia on ammonium perchlorate. This method is stated by Willard[12] to give good results, but owing to the explosive nature of ammonium perchlorate is restricted in its use.

All of these methods, except the first, presuppose the formation of perchlorates and the subsequent liberation of the free acid. In the following experiments the attempt was made to form the acid directly from hydrochloric acid without the intermediate formation of one of its salts.

In oxidizing the chlorine ion to the perchlorate ion it must of course pass through the chlorous and chloric stages. The theory of the formation of the chloric ion and chlorates and the best conditions for effecting this electrolytically are well known. The mechanism of the further electrolytic oxidation of the chlorate to the perchlorate ion was studied by Oechsli[13] in 1903 and more recently in a comprehensive article by Bennett and Mack[14] in

[7] Carpari, Zeit. für angewandte chem., 1893, **6**, 68; Serullas, Ann. de chine et de phys., **45**, 270.

[8] Henry, Lieb. Ann., **31**, 345.

[9] Vorlander and Schilling, Lieb. Ann., 310, 369; Nativelle, J. für prakt. chem., **26**, 404; Van Wyk, Zeit. für anorg. chem., **32**, 115; **48**, 4; Van Ernster, Zeit. für anorg. chem., **52**, 270; Kenny, Thesis, Mass. Inst. Tech.

[10] Kreider, Am. J. of Sc., 3rd series, 1895, **49**, 443.

[11] Mathers, J. Am. Chem. Soc., 1910, **32**, 66.

[12] Willard, J. Am. Chem. Soc., 1912, **34**, 1480.

[13] Oechsli, Zeit. Electrochem., 1903, **9**, 807.

[14] Bennett and Mack, Trans. Am. Electrochem. Soc., 1916, **29**, 323.

1916. The former holds that the perchlorate ion is formed only under conditions of sufficiently high overvoltage to permit the preferential discharge of chlorate ions, which then by secondary reactions with the water form chloric and perchloric acid. Bennett and Mack on the other hand maintain that experimental evidence bears out the view that perchlorate formation is due to the direct oxidation of the chlorate ion by nascent oxygen present in a state of high concentration in an anode at which there exists a high oxygen overvoltage. For a detailed discussion of these two theories Bennett and Mack's paper should be consulted.

Whatever the mechanism of the process may be, the facts seem well established that chlorate ions are most readily oxidized to perchlorate ions in acid solution, at low temperature, high current density and at electrodes, like smooth platinum, which give a high oxygen overvoltage. Chlorate ions on the other hand are more efficiently formed at higher temperatures, lower current densities, and in concentrated solutions.

*Apparatus and Procedure.*—To ascertain the extent to which hydrochloric acid can be oxidized to perchloric acid under varying conditions, a large number of experiments were first carried out in the apparatus described below. This consisted of two concentric cylinders—the inner, a platinum tube 22 cm. long and 0.55 cm. diameter, which served as anode, and the outer of copper 20 cm. long and 6 cm. diameter, which served as cathode. The platinum tube passed through the center of a rubber stopper large enough to close the lower end of the copper cylinder. The stopper and upper parts of the copper tube not in contact with electrolyte were covered with paraffine to prevent corrosion by the action of free chlorine.

The temperature of the cell was regulated by passing a current of water through the anode and up, and around the outer copper cylinder, the whole cell being placed in a beaker.

In series with the cell were an ammeter, a rheostat and a copper coulometer. The voltage across the cell terminals was recorded at intervals by a voltmeter.

Preliminary experiments showed that the amount of perchloric acid produced by the electrolysis of hydrochloric acid depended upon—

1. Duration of electrolysis.

2. Current density on the anode.
3. Concentration of HCl.
4. Temperature of electrolyzing cell.
5. Anode material.

The usual procedure was therefore to keep four of the above factors constant and vary the fifth over a sufficient range. For example, all the above conditions were kept constant except the duration of electrolysis. This factor was varied so that data were secured to determine the products of electrolysis from the time when approximately three ampere-hours had passed, to the time when all the available acid had been converted to perchloric acid. Thus, successive portions of 150 cc. of HCl were electrolyzed at constant current density, acid concentration, temperature and anode material at different values of ampere-hours passed until complete data had been obtained for these conditions.

The next step was to change the current density and make another series of electrolyses, keeping this new value of current density constant with the other factors, while a new set of data was being obtained at various ampere-hours.

When the current density had been varied over a sufficient range, the concentration of the acid was changed and the above described system of runs was repeated with varying current density and ampere-hours for this new concentration of acid.

At the completion of the electrolysis, the electrolyte was removed from the cell and shaken with mercury to remove the free chlorine. After filtering out the mercurous chloride, the filtrate was analyzed for chloride, chlorate, and perchlorate. Three aliquot portions were pipetted off into Erlenmeyer flasks. The first was titrated with one-tenth normal NaOH using phenolphthalein, to give the total acid. The second portion was acidified with $HNO_3$ and titrated for chloride by adding an excess of $AgNO_3$, boiling to coagulate the AgCl and titrating the excess of silver nitrate with ammonium sulpho-cyanate using ferric-ammonium alum as an indicator. The third portion was acidified with dilute nitric acid and an excess of a 10 percent solution of ferrous sulphate added to reduce the chloric acid. After boiling for ten minutes an excess of silver nitrate was added and the chloride-chlorate chlorine determined as before. The perchloric acid was thus determined by difference.

TABLE I.

*Results of Electrolyzing Dilute HCl Solutions, for Different Lengths of Time, at Various Current Densities.*

| Amp. Hrs. | Current density. Amperes per sq. cm | Normality of HCl at start | Normality of HCl at present | Per-cent HCl present | Percent HCl lost by chlorine evolution | Percent HCl converted to $HClO_3$ | Percent HCl converted to $HClO_4$ | Equivalents of $HClO_3$ per liter | Equivalents of $HClO_4$ per liter | Watt hours | Watt hours per gram $HClO_4$ pro-produced |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *Temperature 20° C.* | | | | | | |
| 4 | 0.137 | 0.0984 | 0.0138 | 14.0 | 41.2 | 1.50 | 43.0 | 0.00148 | 0.0423 | 30.0 | 47.4 |
| 5 | 0.137 | 0.0984 | 0.00806 | 8.20 | 43.5 | 1.00 | 48.0 | 0.00098 | 0.0472 | 38.1 | 53.9 |
| 6 | 0.137 | 0.0984 | 0.00384 | 4.00 | 46.0 | ... | 50.0 | ..... | 0.0492 | 46.1 | 62.6 |
| 4 | 0.137 | 0.251 | 0.0500 | 19.9 | 59.0 | 5.38 | 15.0 | 0.0135 | 0.0370 | 22.1 | 39.8 |
| 5 | 0.137 | 0.251 | 0.0310 | 12.4 | 62.0 | 3.75 | 20.0 | 0.0094 | 0.0500 | 28.5 | 38.0 |
| 6 | 0.137 | 0.251 | 0.0200 | 7.98 | 64.0 | 1.99 | 25.0 | 0.0050 | 0.0620 | 35.1 | 37.8 |
| 7 | 0.137 | 0.251 | 0.0110 | 4.38 | 65.4 | 0.50 | 29.4 | 0.0012 | 0.0736 | 41.7 | 37.8 |
| 4 | 0.137 | 0.510 | 0.160 | 31.4 | 60.9 | 6.45 | 2.36 | 0.0329 | 0.0120 | 17.5 | 97.2 |
| 5 | 0.137 | 0.510 | 0.110 | 21.6 | 65.6 | 5.66 | 4.96 | 0.0289 | 0.0253 | 22.6 | 59.6 |
| 6 | 0.137 | 0.510 | 0.073 | 14.3 | 70.2 | 4.90 | 7.61 | 0.0250 | 0.0388 | 28.0 | 48.1 |
| 7 | 0.137 | 0.510 | 0.0550 | 10.8 | 74.9 | 4.12 | 10.2 | 0.0210 | 0.0520 | 33.7 | 43.1 |
| 4 | 0.204 | 0.251 | 0.0570 | 22.7 | 57.0 | 2.15 | 17.9 | 0.0054 | 0.0450 | 27.3 | 40.5 |
| 5 | 0.204 | 0.251 | 0.0390 | 15.5 | 60.0 | 1.39 | 22.4 | 0.0035 | 0.0563 | 35.0 | 41.5 |
| 6 | 0.204 | 0.251 | 0.0290 | 11.6 | 62.5 | 0.70 | 26.8 | 0.0017 | 0.0672 | 43.0 | 42.7 |
| 7 | 0.204 | 0.251 | 0.0200 | 7.97 | 63.0 | ... | 30.1 | ..... | 0.0755 | 51.2 | 45.3 |
| 4 | 0.102 | 0.0984 | 0.0123 | 12.5 | 44.0 | 3.10 | 41.6 | 0.00305 | 0.0410 | 25.8 | 42.0 |
| 4 | 0.171 | 0.0984 | 0.0152 | 15.5 | 38.9 | ... | 45.0 | ..... | 0.0443 | 33.8 | 51.0 |
| 4 | 0.204 | 0.0984 | 0.0157 | 16.0 | 38.8 | 0.60 | 44.0 | 0.0006 | 0.0433 | 37.9 | 58.5 |
| | | | | | *Temperature 40° C.* | | | | | | |
| 3 | 0.137 | 0.217 | 0.0430 | 19.85 | 64.9 | 13.4 | 1.84 | 0.0290 | 0.0040 | 13.5 | 225 |
| 5 | 0.137 | 0.217 | 0.0182 | 8.39 | 72.5 | 13.9 | 6.2 | 0.0280 | 0.0135 | 25.0 | 123 |
| 8 | 0.137 | 0.217 | 0.0020 | 0.92 | 73.5 | 6.0 | 19.6 | 0.0130 | 0.0425 | 44.0 | 69 |

*Results*—The results obtained from a number of typical runs made with this apparatus are shown in Table I. The volume of solution electrolyzed in each case was 150 cubic centimeters. A study of the figures in this table shows:

1. That in dilute solutions, 0.1 *N*, as much as 50 percent of the original acid may be converted into perchloric acid the larger part of the remaining acid being lost as chlorine.

2. That with increasing concentration, the percent which can be thus converted rapidly diminishes, decreasing to 10 percent in half normal solution. The loss as chlorine rapidly increases (approaching 100 percent for concentrations over 1-normal).

3. The percent of chloric acid on the other hand in the electrolyzed liquor increases with increasing initial concentration.

4. Increasing the current density 100 percent (from 0.1 to 0.2 amp. per sq. cm), increases the percentage conversion to perchlorate acid slightly (from 41.6 to 44 percent), while the percentage energy increase is much greater (25.8 to 37.9 watt hours).

5. Increasing the temperature from 20° to 40° tends to decrease the perchlorate acid yield, but increase that of chloric acid present. The energy consumption is at the same time decreased.

With the above results as a guide, the design of a new type of cell was next undertaken in which the oxydation of hydrochloric acid to perchloric could be carried out continuously.

Without entering into the details of the construction and operation of a number of forms of apparatus which developed difficulties for long continued operation, the final form only, which gave excellent service, will be here described.

The form of the cell, shown in Fig. 1, was that of a long, narrow rectangular trough flared at the top. Its dimensions were 18 inches long by 6 inches deep by 1 inch wide (45.7 x 15.2 x 2.5 cm.). It was hammered out of a sheet of silver 30 x 14 x 0.005 inch thick (76 x 35.5 x 0.013 cm.), and was without any seams. This trough which served as the cathode, was reenforced and supported in a copper mesh frame (2 wires to the inch of No. 16 B. & S. gauge (0.13 cm.), to which it was soldered at several points. A silver outlet tube was welded in the bottom of the cell by silver solder. The cell was immersed in a water bath, a strong spray of cooling water being continuously sprayed over both

sides of the cell from perforated pipes placed in the bath. By regulating the rate of flow of the spray, the temperature of the cell could be adjusted within wide limits. Sheet silver was finally chosen for the cell, after copper, iron, nickel, monel, lead and silver plated copper had been tried out, and all found to develop difficulties in long continued electrolysis from the corrosive action of the liberated chlorine.

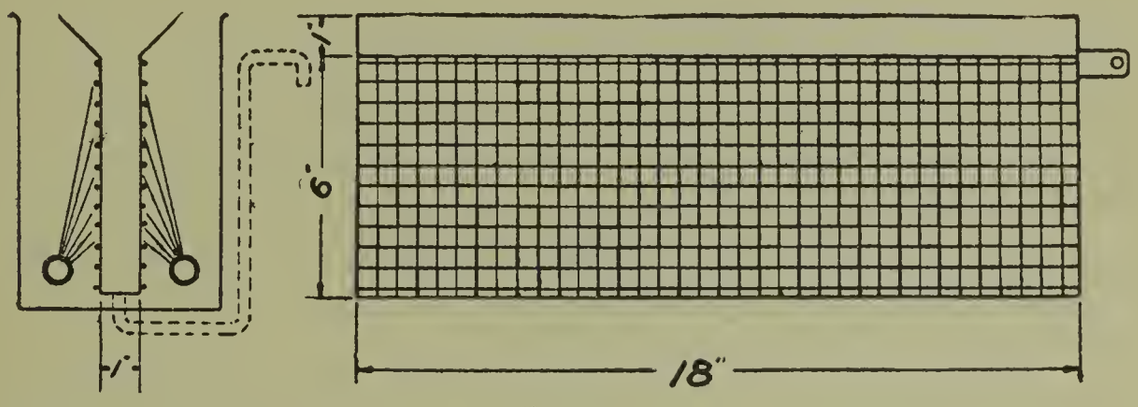


FIG. 1

In the endeavor to find a protective coating which would resist the action of chlorine outside the cell, paraffine, ceresin, shellac, asphalt, asphalt paint and a solution of Grade A Bakelite in amyl acetate were used. Of these the last when properly applied, dried and baked at a temperature not exceeding 150° C., proved very satisfactory.

The anode was of sheet platinum, approximately 5 x 16 inches (12.7 x 41 cm.) in area, and 0.0015 inch (0.0038 cm.) thick, suspended in the center of the cell from a heavy copper rod to which it was clamped. All copper parts and contacts were protected by Bakelite. The anode was held down in place by a glass rod and glass balls attached to the lower edge.

In a continuous run the hydrochloric acid flowed into the cell from a reservoir containing a stock solution and the electrolyzed liquor ran off into two 12-inch fused silica "Vitreosil" evaporating dishes arranged in cascade in which the perchloric acid was concentrated. The flow of the liquid was controlled by an automatic electric regulator, perfected by Messrs. E. C. Walker and F. W. Hall. The evaporation was continued until a 60 percent solution of perchloric acid which boils under atmospheric pressure at 160° C. was obtained. For use in analytical work this solution

was distilled; the product thus obtained contained only a slight impurity of silica accompanied by alumina which probably came from the evaporating dishes.

With a single cell of this type about fifty pounds of 50 percent pure perchloric acid were made during the course of the investigation. The following data taken on one series of experiments illustrate the extent to which the original hydrochloric acid could be converted to perchloric acid.

Initial concentration of hydrochloric acid, 0.5 *N.*
Average current, 150 amperes.
Average voltage, 8 volts.
Average current density (anodic), 0.16 amp./sq. cm.
Average rate of flow of liquor through cell, 2.5 to 3.0 L./Hr.
Average temperature, 18° C.

*Run 1:*

Concentration of HCl at end, 0.0179 *N.*
Concentration of $HClO_3$ at end, 0.0255 *N.*
Concentration of $HClO_4$ at end, 0.0738 *N.*

The product from this run contained too great a percentage of chloric acid. It was therefore brought up to 0.5 normal by the addition of hydrochloric acid and again electrolyzed in the cell. Analysis of the resulting liquor then gave following results:

*Run 2:*

Concentration of HCl at end, 0.0171 *N.*
Concentration of $HClO_3$ at end, 0.0089 *N.*
Concentration of $HClO_4$ at end, 0.2015 *N.*

This solution contained 20 grams of perchloric acid per liter. By again bringing up the acidity and electrolyzing, the solution of the following composition was obtained:

*Run 3:*

Concentration of HCl at end, 0.01117 *N.*
Concentration of $HClO_3$ at end, 0.0078 *N.*
Concentration of $HClO_4$ at end, 0.286 *N.*

In the first and worst case in which the original acid was subjected to electrolysis by passing once through the single cell, a yield of approximately 800 g. of 60 percent acid per 24 hours at an expenditure of 28,800 watt hours or about 26 watt hours per gram of acid (60 percent) was obtained.

There is no doubt but that better results could be obtained by the use of two cells, in the first of which the best conditions for the production of chloric acid were maintained, *i. e.,* fairly strong

acid, high temperature, and medium density, while in the second the products of the first cell would be electrolyzed under the most favorable conditions for the oxidation of chloric to perchloric acid, namely a more dilute solution, low temperature and high current density.

As only one cell was available, however, we were unable at the time to carry out a continuous run under these conditions.

The results obtained with the apparatus demonstrated, however, that a high grade of perchloric acid could be produced in quantity by the electrolysis of hydrochloric acid.[15]

In conclusion, it may be of interest to add that with the acid obtained the salts of the following metals were prepared: strontium, zinc, copper, manganese, nickel, cobalt, iron (ferrous and ferric), tin, bismuth, gold, beryllium and uranium. Perchlorates of ferric iron, aluminum, chromium and magnesium have also been prepared by Weinland and Ensgraber.

These salts are all very soluble in water, and, with the exception of the ferrous, nickel, cobalt and zinc salts, are decidedly hygroscopic. The use of perchlorates, especially of the lead salt, for electroplating purposes is well known from the work of Mathers,[16] as they are very stable and not readily reduced by hydrogen. Ferrous perchlorate is also remarkably stable as regards oxidation.

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[15] The process has since been perfected and used by the Genesee Chemical Co., Batavia, N. Y., for the manufacture of perchloric acid.

[16] U. S. Patent No. 931,944.

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## DISCUSSION.

MAX KNOBEL[1]: This process is in use now by the Genesee Chemical Company. They are making several hundred pounds a year of perchloric acid.

F. A. LIDBURY[2]: Are there any figures on the amount of platinum lost from the anodes?

MAX KNOBEL: There were no data here. I do not have any data on the losses of the Genesee Chemical Company.

ALEXANDER LOWY[3]: Can carbon be used instead of platinum?

MAX KNOBEL: That was attempted, but it disintegrated in the solution, and it was much too difficult to get the carbon out afterwards. The carbon we had did not stand up at all.

C. G. SCHLUEDERBERG[4]: How about graphite?

MAX KNOBEL: Graphite was also disintegrated.

C. H. PROCTOR[5]: Do you know what the Genesee Chemical Company are using it for?

MAX KNOBEL: They are selling it for analytical purposes entirely, I believe.

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[2] Works Manager, Oldbury Electro-Chem. Co., Niagara Falls, N. Y.
[3] Professor of Organic Chemistry, Univ. of Pittsburgh, Pittsburgh, Pa.
[4] Asst. to Manager, Supply Dept., Westinghouse Electric & Mfg. Co., E. Pittsburgh, Pa.
[5] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, September 29, 1921, Vice-President Schluederberg in the Chair.*

# GRAPHIC CONTROL OF ELECTROLYTIC PROCESSES.[1]

By Barzillai G. Worth.[2]


## Abstract.

The control of ion concentration in the solution, according to the author, is of primary importance to electrolytic effects. A graphic method of maintaining fixed conditions in the production of potassium chlorate is presented, high yields depending on relation between three factors: two of which ($A$ and $B$) represent concentrations of two compounds, and a third ($T$), temperature. $B$ is controllable by addition agents. The results of three runs indicate highest chlorate yield with high $A$ reading, second in order with $T$ nearly constant, and lowest yield with falling and rising $T$. [A. D. S.]


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Every electrochemist well knows the difficulty of maintaining the fixed conditions in an electrochemical process which underlie efficiency, and therefore also yield and commercial success. The purpose of the present writing is to show the way in which this problem was handled graphically in a commercial plant, in the hope that it may be of help to others confronted with similar problems.

In the case of potassium chlorate production which we investigated, the end product depends as much on the relations of the various ions in the solution and their solution pressures, bath temperatures, etc., as it does on the essentially electrolytic effects. There is moreover reason to believe that the electrolytic effects are actually secondary in importance, for experience has shown that almost any electrolytic condition brought about by change in

[1] Manuscript received September 3, 1921.

[2] Vice-president, Walter Kidde & Co., Inc., New York City.

electrode material, current density, etc., can be offset and high yield results secured by suitable chemical treatment.

High production therefore depends on the nice balance of different physical factors of the electrolyte. It is comparatively easy to maintain a fixed current density after it has been determined what density is best to use. This is a matter of electrical engineering and power house administration. It is also fairly easy to maintain fixed electrode distances, electrode surface conditions and such like purely mechanical factors, if the maintenance crew are conscientious and efficient. But the control of the ion concentration in the electrolyte is not so easily accomplished, for the indications do not lie on the surface, the remedies must be applied with great care, and many conditions are constantly at work to change these relations.

Let us consider for example a cell (without diaphragm) producing potassium chlorate. In this cell, after electrolysis has proceeded for a period, a considerable number of different ions are reacting on one another. There are the Cl and K, the H and HO, the KOCl and HOCl, and the HCl. Of course, some of these ions and compounds exist for an infinitesimally short time, but the length of time and the effects they have on one another depend on the very nicely balanced laws of mass action.

When a condition of equilibrium between these ions is reached the effect of the current is very regular, the KCl being dissociated and the $KClO_3$ being synthesized at a definite rate. The efficiency depends of course on the respective quantities or concentrations of the various ions which finally come to equilibrium. To establish and maintain the proper concentration for this equilibrium is the problem.

The cell will constantly be losing gases, chlorine, and hydrogen, not to speak of water vapor. Also there is the constant diminution of the KCl concentration and the increase of the $KClO_3$ concentration. It is also difficult in a cell running at high temperature, with varying exterior air temperatures and humidity, to adjust conditions to maintain a perfectly even bath temperature.

This potassium chlorate cell is simply cited as a typical case in order to illustrate the graphic method. The theory and data are conveniently available from actual plant records.

It was found by research in our chlorate plant that the high yields for the particular type of cell, electrodes, and other chemical and electrical features depended principally on the varying relations between three factors: two chemical factors which may be called *A* and *B* (representing concentrations of two compounds in question) and the third factor, the temperature, called *T*. It was calculated from the reactions that in order to get the best results a certain numerical relation must exist between *A* and *B*. *A* was incapable of direct control being the result of establishment of equilibrium, but *B* was controllable by addition agents. Knowing *A* it was possible to compute what *B* should be, which figure was called "Proper *B*" *(PB)*.

Accordingly a system was inaugurated by which the contents of each cell were analyzed daily and the results plotted by weeks. Some of these curves are given herewith. With each curve are tabulated the figures from which the curve was made. Before looking at the curves, study for a moment the tabulated values alone and see how difficult it is to form a logical conclusion as to what is happening and what should be done in any particular case. Four quantities are involved (including *PB*) and it is almost impossible looking at the group of values to gain an accurate idea as to what is the situation, much less the trend. But when one looks at the curves, instantly the trend is apparent, and one knows what changes to make in the cell.

Now looking at the curves, Fig. 1, shows a very satisfactory run (from control standpoint) in which the *B* was kept very close to the *PB*, as it should be. In this case changes in the *A* reading were slow, as *T* was practically constant and the production of chlorate therefore correspondingly uniform, resulting in a fair yield.

Fig. 2 shows a rather odd run. Note how the falling and rising *T* causes a strikingly corresponding change in the *A*. The control did not catch up with these changes and so the *B* ran below the *PB* quite consistently. The chlorate yield of course was lower than in Fig. 1.

Fig. 3 is a graph for a cell operating at a current density different from that of Figs. 1 and 2; therefore, the high *A* reading which runs about 65 instead of 40. The temperature effect is very pronounced. This cell gives a higher chlorate yield than

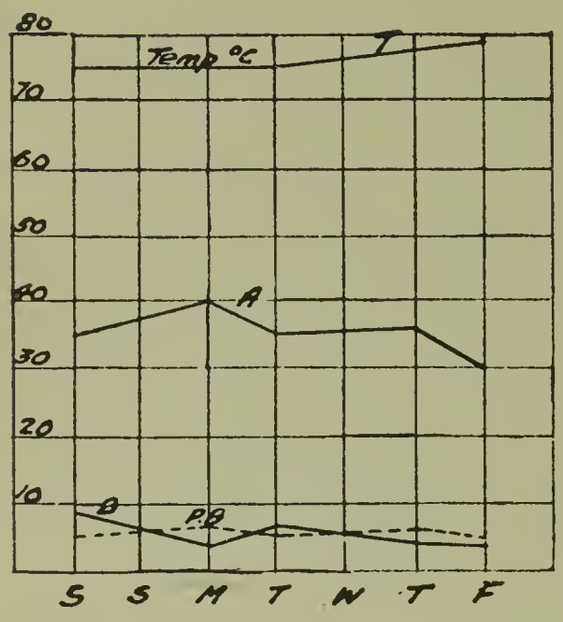


Fig 1

| Day | T | A | B | PB |
|---|---|---|---|---|
| S | 75 | 35 | 9 | 6.0 |
| S | 75 | 37 | 7 | 6.5 |
| M | 75 | 40 | 5 | 7.0 |
| T | 75 | 35 | 7 | 5.5 |
| W | 76 | 35 | 6 | 5.5 |
| T | 77 | 36 | 5 | 6.0 |
| F | 78 | 30 | 4 | 5.0 |

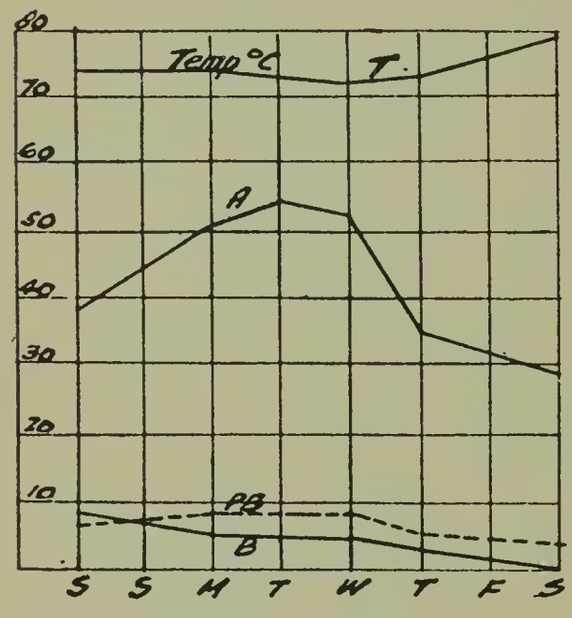


Fig 2

| Day | T | A | B | PB |
|---|---|---|---|---|
| S | 74 | 38 | 8 | 7.0 |
| S | 74 | 44 | 7 | 7.5 |
| M | 74 | 51 | 6 | 8.0 |
| T | 73 | 55 | 5 | 8.0 |
| W | 72 | 53 | 5 | 8.0 |
| T | 73 | 35 | 3 | 6.0 |
| F | 76 | 32 | 2 | 5.0 |

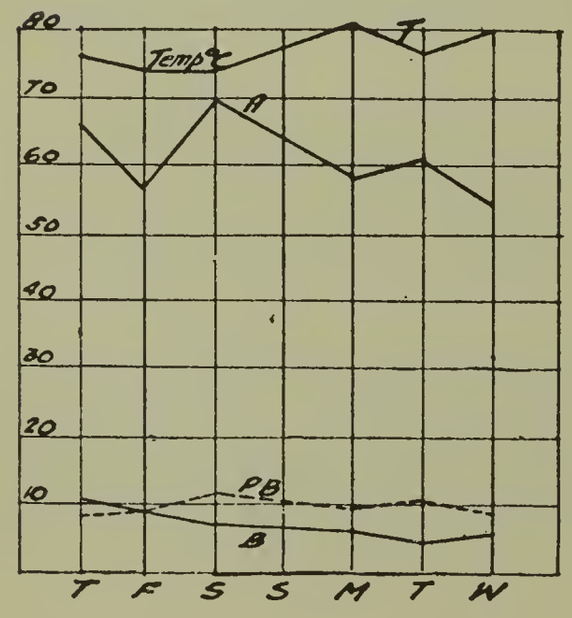


Fig 3

| Day | T | A | B | PB |
|---|---|---|---|---|
| T | 76 | 66 | 11 | 8.0 |
| F | 74 | 57 | 9 | 9.0 |
| S | 74 | 70 | 8 | 7.5 |
| S | 77 | 64 | 7 | 7.0 |
| M | 81 | 58 | 7 | 7.0 |
| T | 77 | 61 | 5 | 5.0 |
| W | 80 | 55 | 6 | 6.0 |

those of Figs. 1 and 2 due to the high *A*. This type of cell is harder to control since the chemical equilibrium is more sensitive than in the cells of Figs. 1 and 2.

From these three curves it is obvious that whenever the *B* does advance or recede beyond a certain point remedial measures should be taken. In practice this was a simple matter, as it necessitated only a change in the rate of feeding addition agents. After a while it became possible to anticipate changes by extending the curve by extrapolation and then making proper changes twenty-four hours in advance, thereby forestalling what otherwise would have been a falling-off of efficiency.

It was not necessary to make a curve of this kind for every cell in the complete plant. Cells, like every other piece of apparatus, have to a certain extent individual characteristics, but they can be grouped into classes, each member of a class functioning practically the same. Two individual members of each of the classes can be sampled to give the graph for the class. Under these circumstances the method of control does not become burdensome, as the number of analyses is not excessive. The different samplings and the analyses can also be handled within certain known limits so as to simplify operations. As a matter of fact, in practice these were brought down to simple titrations and the results obtained so quickly that remedial measures could be promptly applied before conditions changed again, and the control thus became very close.

It may be interesting to state the way in which the addition agents were introduced and affected the *B* concentration, particularly as this was an operation in which the results were secured by a secondary instead of a primary reaction. This datum, however, the writer is not at liberty to include.

The introduction of this system of graphic control was very successful and caused a marked gain in efficiency for the plant. The graph idea was later also applied in a number of other ways.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, October 1, 1921, President Acheson Smith in the Chair.*

# THE EFFECT OF PRESSURE ON OVERVOLTAGE.[1]

By H. M. Goodwin[2] and L. A. Wilson.[3]


## Abstract.

Experiments are described in which the overvoltage of hydrogen against copper, nickel and mercury electrodes was determined under pressures varying from one atmosphere to a few centimeters of mercury. The values were determined by the bubble method, at room temperature, under conditions of very low current density, after a state of constant polarization had been established. The results in all three cases showed a rapid decrease at low pressures, confirming the hypothesis recently advanced by MacInnes and Adler to explain overvoltage phenomena.


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The investigation described below was carried out in 1915. It was expected at the time to continue the work further before publication, but this has not been possible up to the present time. Since, however, the results obtained have been placed at the disposal of Dr. MacInnes[4] and cited by him in support of his theory of overvoltage, it seems desirable to publish a description of the method and procedure by which they were obtained without further delay.

Briefly stated, our investigation was concerned with the effect of pressure on the value of hydrogen overvoltage. The pressures were varied from atmospheric pressure to the vapor pressure of the electrolyte; the cathodes investigated were nickel, lead and mercury and the overvoltage values adopted were those determined by the "bubble" method under conditions of very low and

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[4] Journ. Amer. Chem. Soc., 1919, 41, 194.

constant current densities. The only other experiments published on the influence of pressure on overvoltage are those described by Newbury,[5] who investigated oxygen overvoltage against platinum at pressures varying from 1 to 100 atmospheres and at very high current densities. The purpose of his work and the conditions under which it was carried out were so different from ours that the results of the two investigations have little in common.

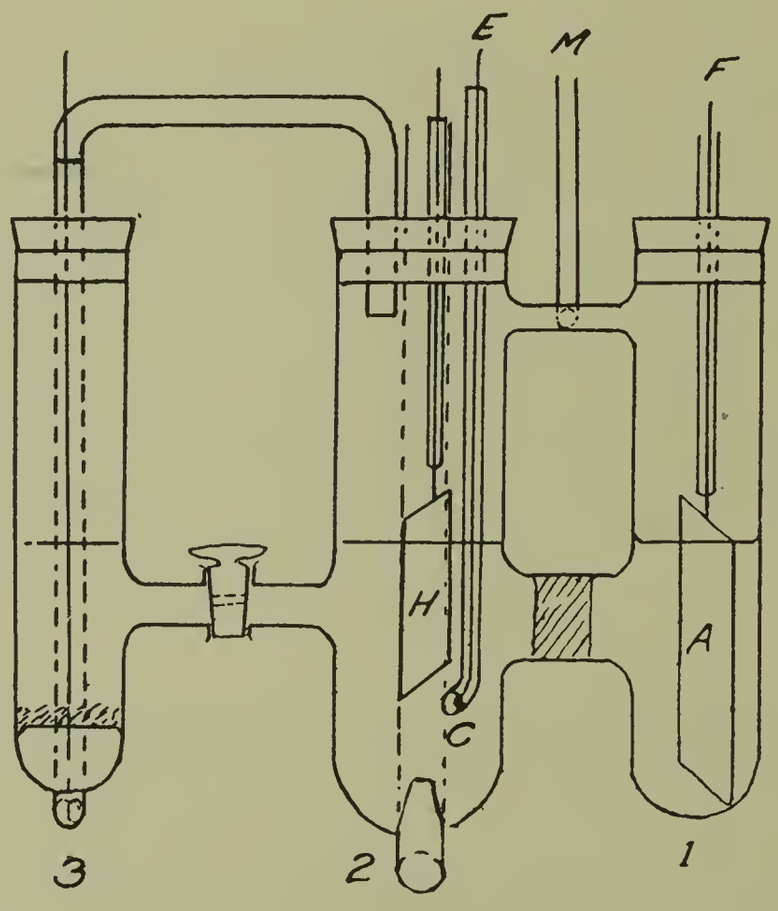


FIG. 1

The general procedure followed in the work was to measure directly the difference of potential between a reversible hydrogen electrode and a cathode on which bubbles of hydrogen gas were just beginning to be liberated at a definite measured rate, both electrodes being under identical conditions as regards temperature, pressure of hydrogen gas, and electrolyte. To obtain concordant results, the well-known difficulties inherent in over-

[5] Journ. Amer. Chem. Soc., 1914, **105**, 2429.

voltage measurements had to be carefully guarded against. The form of apparatus and other essential details of the procedure are described below:

The design of the cell used is shown in Fig. 1. It consisted of three glass tubes sealed together with side arms in the manner indicated. The anode A of platinized sheet platinum was placed in 1; the cathode C under investigation and the reference hydrogen electrode H were placed in 2; a mercury-mercurous sulfate reference electrode was introduced into 3. The anode and cathode compartments were separated by a plug of cotton wool to diminish diffusion of the anolyte to the cathode.

Compartments 2 and 3 were connected by a glass stopcock which was opened only when a control measurement was being taken with the mercury electrode. Hydrogen gas generated by electrolysis and very carefully purified was introduced into the cell through a tube sealed into the lower end of 2. The pressure of the gas in all three compartments was the same and was measured by a mercury manometer connected at M. The electrolyte throughout the cell was $2N$ sulfuric acid.

The source of electromotive force used for the electrolysis was obtained from a storage battery connected through a drop wire (Drumbridge). It was applied to the terminals E, F. The current through the cell was calculated from the potential drop measured on a potentiometer, through a standard 100,000 ohm resistance connected in series. The difference in potential between the cathode C and the hydrogen electrode H (or mercury electrode) was measured directly with a potentiometer and a galvanometer sensitive to less than 0.0001 volt.

The whole apparatus was immersed in a water bath with plate glass sides, the temperature of which was maintained constant at 25° C. to within one hundredth degree by means of a current of water from an electrically regulated thermostat. Observations on bubble evolution were made by means of a horizontal low power microscope. To facilitate these observations the surface of the cathode was strongly illuminated by means of light concentrated upon it by a total reflecting glass rod. Bubbles 0.02 mm. in diameter could be easily observed.

The pressure within the whole apparatus could be reduced

to that of the vapor pressure of the electrolyte by means of a rotary mercury pump.

The greatest difficulty was encountered in constructing electrodes which would give reproducible results. The slightest trace of grease, oxide or foreign material in contact with the electrode is sufficient to introduce uncertainty and irregularities in the bubble point. Thus electrodes coated with asphalt or enamel were found to give fluctuating values. After much experiment-

FIG. 2

ing, electrodes made in the following way gave very satisfactory results and can be recommended for work of this character. A thick walled glass tube, two or three millimeters inside diameter was drawn out and bent as shown in Fig. 2, the bore at the open end A tapering slightly towards the bend. The open end was ground off flush and smooth. A piece of the metal to be studied in the form of a cylinder was then turned or filed down to approximately the same taper as A. It was then ground into the glass

tube with fine carborundum powder and water until it fitted so perfectly that no liquid could be drawn between the two by suction. A short piece of fine platinum wire attached to the inner end of the electrode served to make contact between it and the leading in wire B. After the electrode was ground to fit its glass container the outer end was filed off flush with the glass and the whole end then ground down on a plate of frosted window glass until perfectly smooth. The electrode was then completed by connecting it with the lead B by means of a drop of mercury as shown in the figure. An air pocket between the mercury and electrode must be avoided to prevent the mercury being forced up the tube when the apparatus is exhausted.

Electrodes prepared in this way presented a circular surface, the area of which could be readily calculated from measurements of its diameter. They were as nearly clean and free from contact with any foreign material other than glass as it was possible to make them. Bubbles usually formed near the glass, but never at the contact between the metal and its surrounding sheath, as was the case when rubber, paraffine or sealing wax coatings were used. The bubbles were evolved one at a time with great regularity. The construction of reproducible mercury electrodes of known area is more difficult and at best unsatisfactory, owing to the film of liquid held by capillarity between the contact surface of mercury and its container. We obtained the best results with electrodes of the type used by Lewis and Jackson[6] adjusting the surface of each fresh drop until it was hemispherical in form. The effective cathode area is, however, always greater than the area of the exposed hemisphere and is more or less variable owing to the formation of bubbles between the glass and mercury.

As the decomposition point at mercury cathodes as indicated by the "bubble point" depends upon whether gas has or has not been previously evolved at the surface,[7] *i. e.*, whether observations are made along an ascending or descending current—potential decomposition curve, special precautions were necessary to obtain concordant results. Thus it was found there was a difference as great as 0.08 volt between the point at which bubbles were

[6] Zeit. für Phys. Chem., 1906, **53**, 193.

[7] This is undoubtedly due to the necessary presence of hydrogen nuclei, in or on the electrode, for the formation of bubbles, as emphasized by MacInnes.

formed on a freshly formed mercury cathode with increasing applied e. m. f., and that at which they ceased to be evolved after the decomposition point had been passed and the e. m. f. was gradually diminished.

In the following experiments the approximate decomposition point was first determined by preliminary measurements. When this point was nearly reached in the final experiments, the applied e. m. f. was increased very gradually, 0.005 volt at five-minute intervals, until bubbles became visible. They were usually

TABLE I.

*Overvoltage of Nickel at Varying Pressures.*

Area of Electrode Surface, 0.049 sq. cm. Temperature 25°C.

| Time (hours) | $E_h$ (volts) | 1 x $10^{-6}$ (amp.) |
|---|---|---|
| Total pressure = 87.26 cm. mercury. | | |
| 10.00 | 0.1265 | 0.3566 |
| 10.15 | 0.1241 | 0.3363 |
| 10.30 | 0.1243 | 0.3367 |
| 11.00 | 0.1244 | 0.3368 |
| Mean | 0.1248 | 0.3416 |
| Deviation | 0.004 | 0.0025 |
| Pressure 76.44 cm. | | |
| 4.40 | 0.1262 | 0.3605 |
| 4.50 | 0.1265 | 0.3605 |
| 5.00 | 0.1262 | 0.3594 |
| 5.50 | 0.1265 | 0.3569 |
| Mean | 0.1264 | 0.3593 |
| Deviation | 0.0001 | 0.0004 |
| Pressure 65.03 cm. | | |
| 3.00 | 0.1280 | 0.3146 |
| 3.15 | 0.1287 | 0.3146 |
| 3.30 | 0.1293 | 0.3149 |
| 3.45 | 0.1296 | 0.3171 |
| 4.00 | 0.1294 | 0.3178 |
| 4.30 | 0.1286 | 0.3118 |
| 5.10 | 0.1287 | 0.3162 |
| Mean | 0.1290 | 0.3153 |
| Deviation | 0.0002 | 0.0006 |

TABLE I—*Continued.*

| Time (hours) | $E_h$ (volts) | 1 x $10^{-6}$ (amp.) |
|---|---|---|
| **Pressure 52.82 cm.** | | |
| 10.50 | 0.1344 | 0.3344 |
| 11.00 | 0.1346 | 0.3286 |
| 11.10 | 0.1345 | 0.3269 |
| 11.20 | 0.1354 | 0.3260 |
| 11.30 | 0.1342 | 0.3276 |
| Mean | 0.1344 | 0.3287 |
| Deviation | 0.0001 | 0.0011 |
| **Pressure 42.31 cm.** | | |
| 12.00 | 0.1568 | 0.3775 |
| 12.30 | 0.1582 | 0.3693 |
| 1.00 | 0.1597 | 0.3723 |
| 1.30 | 0.1581 | 0.3716 |
| 2.00 | 0.1584 | 0.3715 |
| Mean | 0.1582 | 0.3724 |
| Deviation | 0.0003 | 0.0009 |
| **Pressure 3.45 cm.** | | |
| 10.50 | 1.0039 | |
| 11.00 | 1.0115 | 0.3151 |
| 11.05 | 1.0161 | 0.3120 |
| 11.10 | 1.0086 | 0.3128 |
| 11.15 | 1.0096 | 0.3129 |
| Mean | 1.0099 | 0.3132 |
| Deviation | 0.0012 | 0.0005 |

evolved at the rate of about three per minute. The applied e. m. f. was then lowered until the rate of evolution was two bubbles per minute—when the cathode potential against the hydrogen electrode was measured. This point, although arbitrary, was chosen as a convenient rate of gas evolution at which to compare the overvoltage values in all our experiments. A slower rate becomes time consuming, while a higher rate leads to too high values. In the interest of uniformity it is highly desirable that some standard conditions for taking observations of this phenomenon be adopted. In all cases they should at least be definitely stated.

In the following tables are given the observed values of overvoltage, $E_h$, corresponding total pressures, current and time, all measurements being made at 25° C. The vapor pressure at this

TABLE II.

*Overvoltage of Lead at Varying Pressures.*

Area of Electrode Surface, 0.0033 sq. cm.

| Time (hours) | $E_h$ (volts) | 1 x $10^{-6}$ (amp.) |
|---|---|---|
| **Pressure 78.36 cm.** | | |
| 6.00 | 0.6754 | 0.4513 |
| 6.15 | 0.6776 | ..... |
| 7.30 | 0.6721 | ..... |
| 7.45 | 0.6728 | ..... |
| 8.00 | 0.6726 | .... |
| Mean | 0.6741 | ..... |
| Deviation | 0.0009 | ..... |
| **Pressure 36.16 cm.** | | |
| 8.45 | 0.6836 | ..... |
| 9.00 | 0.6864 | ..... |
| 10.15 | 0.6838 | 0.4513 |
| 10.30 | 0.6852 | ..... |
| Mean | 0.6848 | ..... |
| Deviation | 0.0006 | ..... |
| **Pressure 28.14 cm.** | | |
| 3.00 | 0.8036 | ..... |
| 3.15 | 0.8042 | ..... |
| 3.30 | 0.8055 | ..... |
| 4.00 | 0.8048 | 0.4513 |
| 4.45 | 0.8032 | ..... |
| Mean | 0.8045 | ..... |
| Deviation | 0.0004 | ..... |

temperature of a $2N$ sulfuric acid solution is approximately 2.2 cm. The partial pressure of hydrogen is therefore the recorded pressure minus 2.2 cm.

Each series of measurements extended over several hours, but only those measurements which were recorded during the last

hour or two when the overvoltage had reached a steady value are here given. It is to be noted that when eqilibrium has been attained the overvoltage remains constant to within a few tenths of one percent for a period of from one to two hours.

TABLE III.

*Overvoltage of Mercury at Varying Pressures.*

Area of Electrode Surface, 0.049 sq. cm.

| Time (hours) | $E_h$ (volts) | 1 x $10^{-6}$ (amp.) |
|---|---|---|
| **Pressure 78.36 sq. cm.** | | |
| 7.00 | 0.7677 | .... |
| 7.15 | 0.7664 | .... |
| 7.30 | 0.7623 | 2.062 |
| 7.45 | 0.7658 | .... |
| 8.00 | 0.7608 | .... |
| Mean | 0.7656 | .... |
| Deviation | 0.0022 | .... |
| **Pressure 36.16 sq. cm.** | | |
| 9.30 | 0.7645 | .... |
| 9.45 | 0.7686 | .... |
| 10.00 | 0.7680 | 2.062 |
| 10.30 | 0.7643 | .... |
| 10.45 | 0.7682 | .... |
| Mean | 0.7667 | .... |
| Deviation | 0.0019 | .... |
| **Pressure 23.89 sq. cm.** | | |
| 4.00 | 0.9630 | .... |
| 4.30 | 0.9645 | .... |
| 4.45 | 0.9647 | 2.062 |
| 5.00 | 0.9653 | .... |
| Mean | 0.9644 | .... |
| Deviation | 0.0006 | .... |

The above results are shown graphically in Figs. 3, 4 and 5. It will be seen in all three cases investigated that the overvoltage increases rapidly when the pressure is decreased to very small values. The

general form of the overvoltage pressure curve is that of an hyperbola. At the time these results were obtained, no satisfactory explanation of them was apparent. Recently, however, MacInnes and Adler in a very interesting paper[8] have deduced

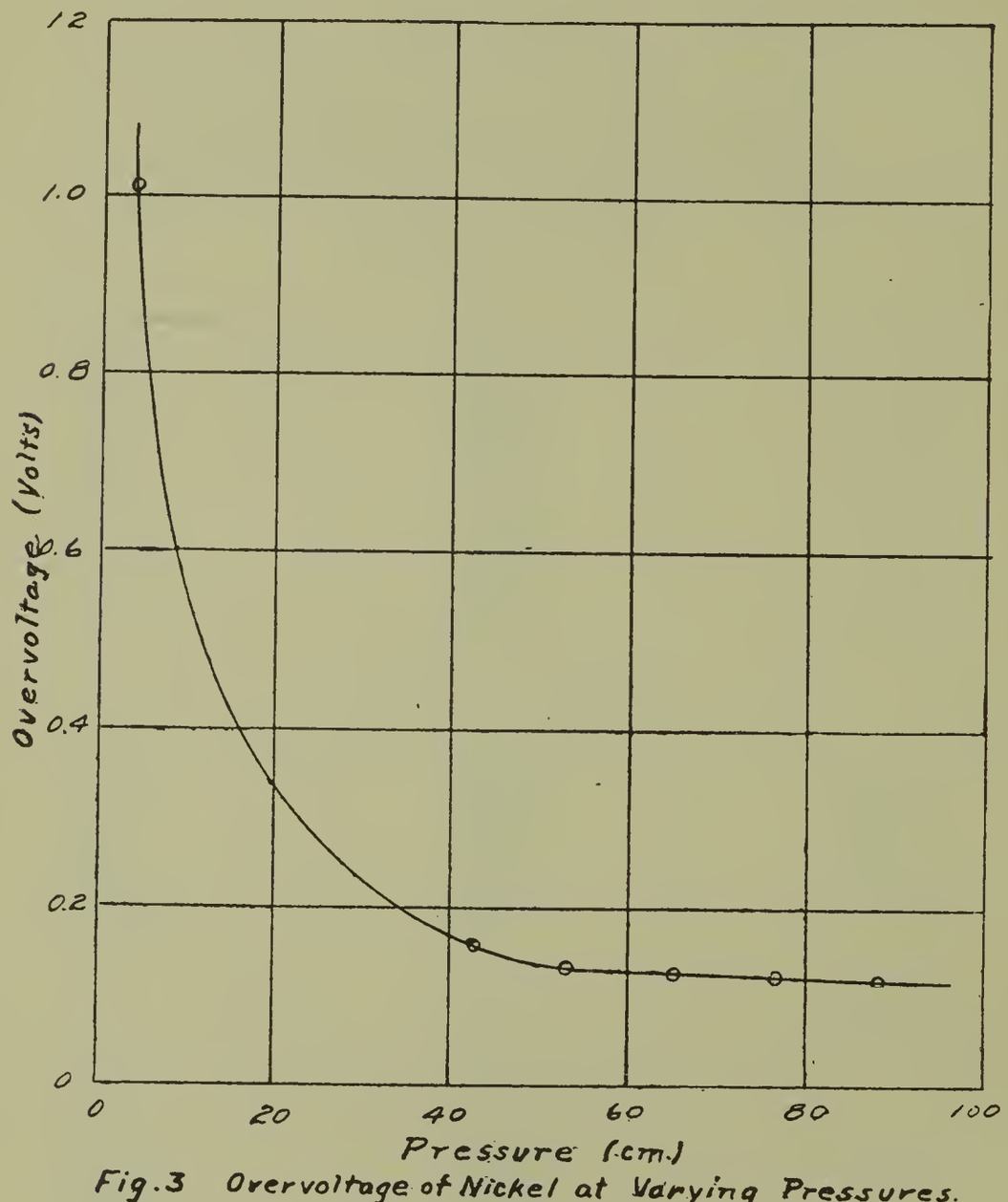


Fig. 3 Overvoltage of Nickel at Varying Pressures.

the following relation between the overvoltage E and the pressure p, under which the bubbles are evolved:

$$E = \frac{3\,R\,T\,\gamma}{2\,F\,r} \cdot \frac{1}{p}$$

in which $\gamma$ is the surface tension and r the radius of the bubble, F, the Faraday, T the absolute temperature, and R the gas con-

[8] Journ. Amer. Chem. Soc., 1919, 41, 204.

stant. If the radius of the bubbles is independent of the pressure, *i. e.*, may be regarded as constant for a given electrode under constant rate of gas evolution, $E = \frac{K}{p}$ or $E.p$ = constant at constant temperature, and the curve connecting E and p should be an equilateral hyperbola. MacInnes proved by direct experiments in the article referred to that the radius of hydrogen bubbles does

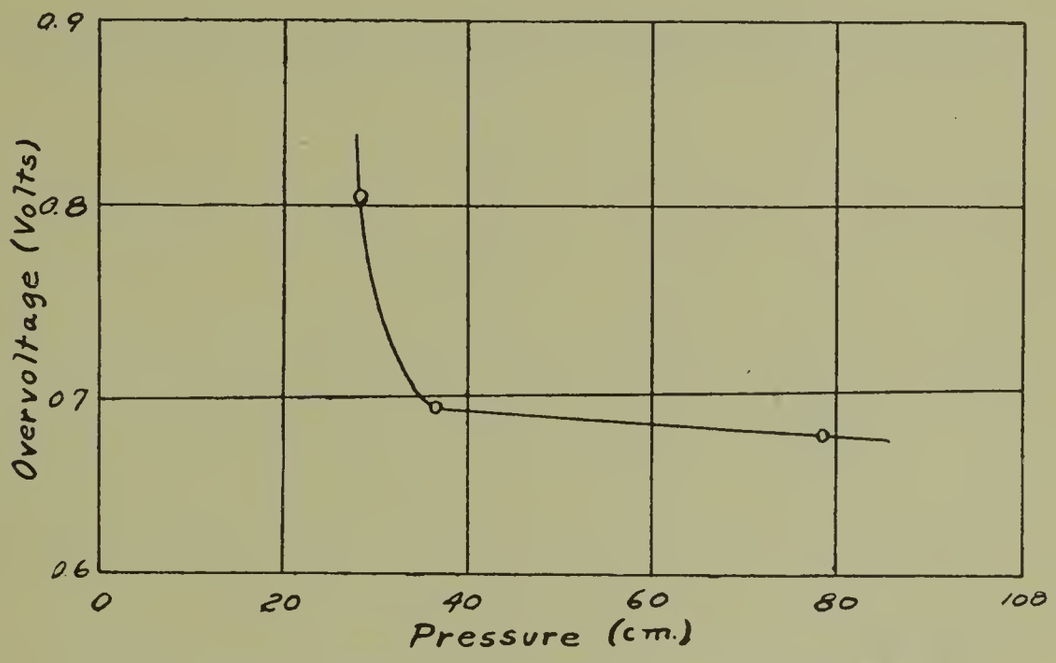


Fig 4 Overvoltage of Lead at Varying Pressures.

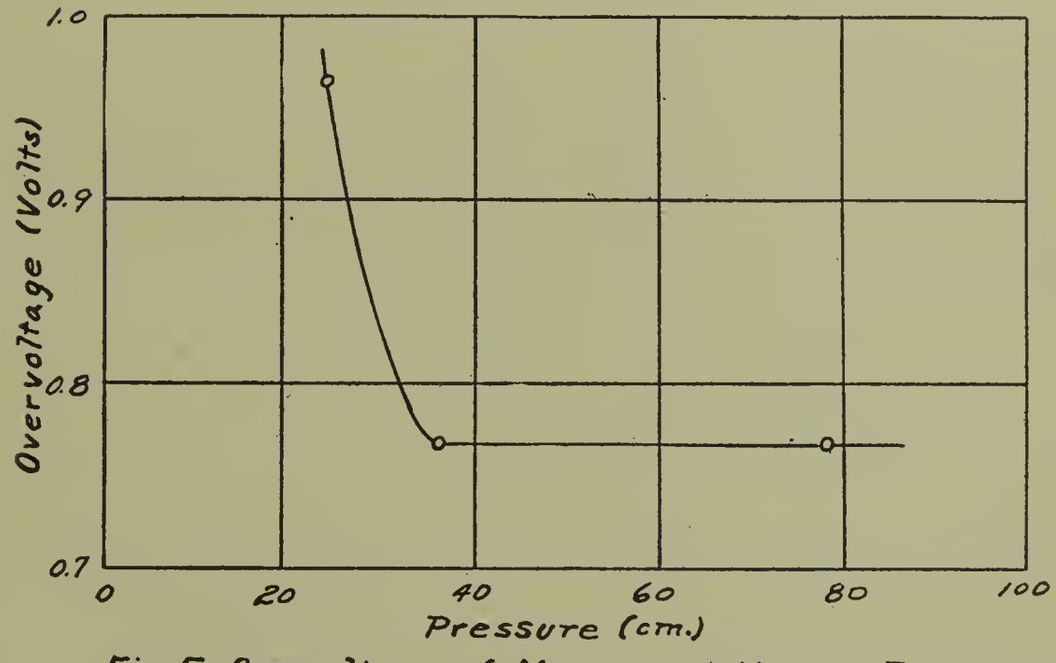


Fig. 5 Overvoltage of Mercury at Varying Pressures.

not vary when the pressure is increased from 1 to 16 atmospheres. Hence the above formula and the hypothesis on which it is based is strikingly confirmed by the results of our work.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, October 1, 1921, President Acheson Smith in the Chair.*

# RESEARCHES ON THE ELECTRODEPOSITION OF IRON.[1]

By W. E. Hughes, B. A.[2]

## Abstract.

After some general remarks the author considers first, at length, the electrodeposition of iron from I Sulphate Solutions, II Chloride Solutions, III Sulphate-Chloride Solutions, stating the results obtained by different workers and of his own work on the different baths. He then discusses various researches upon other solutions than these, with his own experiences and comments. [J. W. R.]

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## General Remarks.

A careful consideration of the numerous solutions proposed for the deposition of iron makes the following matters clear:

1. The solutions proposed may (with some few exceptions) be divided into three groups, namely, (I) those based upon the use of sulphate of iron; (II) those based upon the chloride, and (III) those containing both sulphate and chloride.

2. Ferrous salts alone serve any useful purpose.[3]

3. The employment of organic salts or "addition agents," *e. g.*, gums, gelatin, glycerin, is unnecessary.

4. A difference of opinion exists as to whether the solution should be neutral or acid.

5. The object for which the electro-deposit is required must be considered when fixing upon the type of bath to employ. A

[1] Manuscript received April 25, 1921. Presented with the permission of the Council of the Department of Scientific and Industrial Research, London.

[2] Electrometallurgist, London, England.

[3] Watt's work is especially instructive on this point. (*v.* The Electrician, Nov. 11 and 25, Dec. 16 and 30, 1887, and Jan. 13, 1888); and *v.* G. Gore Electrometallurgy, 1906, p. 245 (Longmans).

bath that would do quite well for steel-facing might be quite unsuitable for refining, and *vice versa.*

*The Relative Values of the Sulphate and Chloride Baths.*

The chloride bath certainly has advantages over the sulphate solution in the following respects:

(a) It can be made more concentrated on account of the greater solubility of chloride of iron; it can, therefore, contain more metal—iron.

(b) It is a better conductor of the current, generally speaking. Hence, a lower voltage is required, and the bath is, thus, cheaper to work.

(c) In general, the rate at which the chloride bath can be worked, *i. e.,* the current density employable, is, *ceteris paribus,* greater than in the case of the sulphate solution.[4]

On the other hand, the sulphate bath is preferable to the chloride solution in the following respects:

(a) It can, in many cases, be worked at the ordinary temperature, and can always be worked at a temperature not much above normal,[5] whereas chloride baths almost always require a much higher temperature. (*cf.* Merck's and the Fischer-Langbein baths).

(b) The oxidation of the solution is, in almost all cases, less.

(c) The deposits oxidize very much less quickly than do deposits from the chloride baths. This seems generally recognized by those who have worked with both types of baths. The present author's experience is that the ease with which its deposit rusts is the worst feature of the chloride bath.

*The Chloride-Sulphate Baths.*

This third group of solutions for iron deposition includes some baths which appear to have given great satisfaction to their

[4] Schlötter's sulphate bath and process appears to form an exception; but Schlötter's process is as yet untried. Moreover, this statement is intended to be a general one.

[5] It is not to be inferred that the sulphate bath gives its best results at the lower temperature. Pfaff, Foerster, and others, recommend working at 70° C., or above, even with the sulphate solution. Schlötter recommends nearly boiling temperature. Foerster says: "While iron-nickel alloys are inclined to peeling at the cathode, pure iron can be obtained as a well-adhering finely crystalline, iron gray deposit, by the electrolysis at 80° C. and a current density of 2 amp/sq. dm. of a solution containing 10 g. Fe per 100 cc. using wrought iron anodes." Zeit. f. Elektrochemie, 1897, 4, 163. But *v.,* per contra, Russ and Bogomolny, Zeit. f. Elektroch., 1906, 12, 697.

authors, *e. g.,* Varrentrapp's, Watts and Li's, and others. The great objection to "mixed" electrolytes is, in the author's opinion, the difficulty of control, whether scientific or practical, especially on the anode side of the bath. With both chloride and sulphate in the solution it is almost impossible to know what the reactions, chemical and electrochemical, will be at the anode. And, from the practical point of view, though a bath of a complex composition may give good results for a time, it will not always do so (no bath does), and, when something "goes wrong," it will be much more difficult to ascertain what the trouble is and, when found, to put things right. Simplicity of composition must, therefore, always be advisable where it can be obtained. Hence, where two solutions, one simple and the other complex, give approximately the same good results, the simple one is to be preferred. In the case of iron baths, some of those containing only one anion give quite as good results as any of those containing more than one; there is, consequently, no reason to use one of the latter. Doubtless the author's objection to complex baths applies to the anode rather than to the cathode side, but it is a very great mistake to neglect the phenomena that occur at the anode. These may, and often do, affect the result obtained at the cathode, as is clearly seen in the case of the silver-plating bath—an extreme case, indeed, but an instructive one.[6]

### *Acid vs. Neutral Baths.*

The author's view, based upon long experience, is that very slight acidity is beneficial, at any rate in the case of the sulphate baths. Slight acidity hinders oxidation of the solution, and prevents the formation of basic salts at the cathode. It, further, improves the conductivity, and enables a considerably higher current density to be employed without injury to, and frequently to the benefit of, the deposit; but s l i g h t acidity is all that should or, indeed, can be employed. If any considerable quantity of free acid be present, the cathode efficiency suffers in a marked manner; loss of efficiency is scarcely noticeable with slight acidity. Moreover, the presence of considerable free acid causes a distinct

[6] *Cf* Steinbach-Buchner, Die Galvanischen Metallniederschläge, 2nd edition, 1896, p. 79 *et seq.* Störungen in der Arbeit des Silberbades.

diminution in the size of the grains of which the deposit consists, accompanied by a distinctly increased hardness and brittleness. In the case of the chloride bath, the author's experience is that the change in grain size produced even by very slight acidity (HCl),[7] and the accompanying increase in hardness and brittleness are so great that it is advisable to keep the bath neutral during working. Rather than employ acid to hinder oxidation it is better to effect this object by the use of some alkali chloride which will form a double salt with the ferrous chloride, as is done in the case of the Fischer-Langbein bath.

### *The Purpose of the Deposition.*

The purpose for which the deposit is required is, usually, not sufficiently borne in mind, when this or that solution is adopted for obtaining an iron deposit. Yet it is essential that the solution should suit the desired object. For instance, it is to no purpose that a bath containing organic salts or other like substances is selected for the deposition of p u r e iron.[8] However fine the deposit may look macroscopically, it will certainly be impure. Again, a solution used for steel-facing must be one that will give a thin layer of very hard iron. Color is unimportant in this case, as also is thickness. A deposit that would be of sufficient thickness for steel-facing will often crack up and peel off the base metal, if deposition be continued. In other words, a solution giving such a deposit, though quite suitable and useful in a printing works, would be useless in a refinery. Instances need not be multiplied. The truth is that, as in the case of solutions used for the electrodeposition of other metals, nickel, zinc, tin and others, no one iron solution is of what may be called the "universal" type, or one suited to every purpose. Even the acid copper bath—the most adaptable of all the solutions used for the deposition of metals—must be varied in respect of the relative amounts of copper sulphate and acid it contains. A bath containing proportions of these substances suitable for electrotype work would be quite unsuitable for producing a thick, smooth deposit on a printing roller.

[7] *v.* W. E. Hughes, Trans. Faraday Soc., 1921.

[8] *Cf.* the work of R. Kremann and his collaborators, post.

## Group I.

### SULPHATE SOLUTIONS.

### (1) *C. Hoepfner and Klie's Solution.*[9]

These investigators do not appear to have published anything respecting their work on iron deposition; information regarding it has to be obtained from other sources.

K. Arndt states of the work of Hoepfner and Klie, "Dr. Klie has in 1895 deposited iron under the following conditions: *Bath*—A weakly acid solution of 462 grams $FeSO_4$ + 75 grams $(NH_4)_2SO_4$ in 1.5 lit. water. *Cathode*—Copper sheet, rubbed with vaselin and sprinkled over with powdered graphite. *Anode*—Cast iron plate. *Diaphragm*—Thin porous plate inserted in a frame between the anode and cathode. The bath temperature was maintained at 70° to 80° C., the current density was about 3 amp./sq. dm., and the voltage amounted to 0.75 volt."

Arndt mentions that the process was not followed up, as no economic use for chemically pure electrolytic iron was present to Hoepfner's mind.

### (2) *Klein's Solution.*

The solution which is usually referred to as "Klein's" is one that is based upon ferrous sulphate, as the metal salt, and contains magnesium sulphate, as the conducting salt. The present author cannot find in the literature any details of the bath published by Klein himself; but information respecting it has been given by others.[10]

(*a*) *F. Haber on Klein's Solution.*[11] This authority states that he obtained faultless deposits from Klein's bath under the following conditions: *Composition*—0.5 g. mole. of $MgSO_4$ *aq.* and the same weight of $FeSO_4$ *aq.* to each liter of water. *Current density*—0.25 amp./sq. dm. *Cathode*—Lacquered sheet (copper). He found that when he deposited the iron upon a stationary copper cylinder, suspended within an iron tube (which served as anode), the deposit showed a tendency to split up; but that if

[9] The details given are taken from K. Arndt, Zeit. f. Elektrochemie, 1912, **18**, 233.

[10] Unless the information contained in English patent No. 2456 (1869), taken out by M. H. Jacobi and E. Klein be considered as a publication of details of his bath by Klein himself. See also M. H. Jacobi, Bull. de l'Acad. Imper. des Sci. de St. Petersburg, 1869, **13**, 40 and *Ibid.*, Brit. Assoc. Rep., 1869, 67.

[11] Zeit. f. Elektrochemie, 1898, **4**, 413.

the cathode cylinder was rotated, deposits up to 0.15 mm. thick could be obtained (and at the relatively high current density of from 0.4 to 0.42 amp./sq. dm.) without any sign of peeling. The same author describes "clichés" (printing plates) which he had seen and which were prepared for the printing press of the Austro-Hungarian State Bank. They were used for printing bank-notes. The solution used to prepare them was either Klein's or some slightly modified form of Klein's. The conditions of deposition were kept secret; but, Haber remarks that the rate of deposition must have been slow, since a plate of about 2 mm. thickness required 1.5 months for its preparation. The deposit was, even on the back side, equal to carefully deposited copper sheet of equal thickness. It showed no pits.

(*b*) *S. Maximowitsch on Klein's Solution—Modified.*[12] Maximowitsch, electrochemist to the Royal Expedition for the preparation of State Papers at St. Petersburg, gives the following particulars of the bath for iron deposition employed by him, and of its preparation. This bath is either the same as Klein's or very like it, for Klein was engaged on the same work and at the same place as was Maximowitsch. An accumulator cell, of six litres content, was filled with a solution of 20 percent. $FeSO_4$ *aq.* and 5 percent $MgSO_4$ *aq.*, and two iron electrodes (20 x 15 cm.) were suspended in it. The cathode was a copper plate, lightly "silvered and iodized." Twenty-five grams of $NaHCO_3$ were added to the solution. This caused a dirty yellow foam to form on the surface which changed after three days into a brown skin. The solution gradually cleared, with the separation of a voluminous precipitate. Twice a week, from 20 to 25 grams of the bicarbonate were added, and this was continued for four weeks, by which time some 186 grams of bicarbonate had been added, which was sufficient to precipitate the iron from 300 grams $FeSO_4$ *aq.*, that is from 25 percent of the total amount of iron salt used. Under the skin of ferric hydrate the solution was protected from atmospheric oxidation, and became quite clear. The content of $Fe(CO_3H)_2$ was found to be 0.23 percent.

As regards the deposition, Maximowitsch says: "After the first addition of bicarbonate, the circuit was closed, and it was only

[12] Zeit. f. Elektrochemie, 1905, **11**, 52. For some observations on Klein's bath, see also H. Lee. Abhandl. d. Deutsch. Bunsen—Gesellschaft, Nr. 2.

broken every two or three days for control purposes. The current density varied from 0.2 to 0.3 amp./sq. dm.[13] The deposit was at first light grey, and showed no inclination to peel; but it was brittle—indeed, friable (*mürbe*). The deposit was found to become more and more tough and flexible, until after four weeks, the bath reached its optimum. The iron then obtained proved quite exceptionally suited to the preparation of printing plates. It attained a tensile strength of 5,180 kg./sq. cm., yet, withal, was so flexible that it could be sharply bent without breaking. Its surface had a beautiful silk-grey color, and was free from pits. The best current density was 0.3 amp./sq. dm.; the maximum, 0.6 amp./sq. dm. High current efficiency (97 to 99 percent) was notable."

Maximowitsch states further that the bath deteriorated in its results after a time, the deposits becoming brittle and pitted. He found, however, that by passing pure $CO_2$ into the solution the bath almost recovered its former excellence, and in this way he maintained his iron bath in good condition over a long period.

*Remarks:* The present author has found that by following Maximowitsch's instructions a most excellent deposit can be obtained.[14] It is of a silver grey color and obviously crystalline. It is very adherent, flexible, and shows no pitting. No nodules are formed. Furthermore, the bath gives little or no trouble in working. He found that at a temperature of 30° C. the current density could be raised to 0.5 amp./sq. dm. for continuous deposition over five days and nights, a very fine deposit being obtained. As the bath is slow (on account of the low current density employable), it can be useful for a limited number of purposes only. Nevertheless, the results that can be obtained from it are so good, and the number of uses to which the bath can be put is so considerable, that it was thought well to consider the solution in some detail.

It must be mentioned that Pfanhauser remarks that he could not obtain ductile iron by following Maximowitsch's instructions. Pfanhauser seems to think that the reason for the deposition of

[13] This C. D. requires a voltage of about one volt for an electrode distance of 20 cm., working at 18° to 20° C. (*v.* W. Pfanhauser, Galvanotechnik, 1910, p. 613).

[14] Russ and Bogomolny also obtained good results. For an account of their work on Klein's bath, see post.

ductile iron from this bath, should it occur,[15] would lie in the fact that the hydrogen bubbles can be evolved instead of being "taken up" by the iron (perhaps to form an alloy with it), as happens in other baths used, at ordinary temperature, for iron deposition.

(*c*) *M. H. Jacobi*[16] and also *W. C. Roberts-Austen*[17] give some interesting accounts of Klein's bath. It seems that Jacobi, who worked out the bath with Klein, worked for some days at the Royal Mint, and communicated details of the methods of manipulation of the bath to Roberts-Austen, who in the following year (1870) visited St. Petersburg, and saw the iron deposition at work on a large scale. He states that it was being employed in the preparation of plates "to be used for printing the paper money of Russia."

### (3) *C. F. Burgess and C. Hambuechen's Solution.*[18]

These authors write as follows: "The electrolyte consists of ferrous and ammonium sulphates; the current density at the cathode is 6 to 10 amp./sq. ft. (0.66 to 1.11 amp./sq. dm.) and at the anode slightly less; the electromotive force for each cell is slightly under one volt; the temperature of the electrolyte is about 30° C.; the anodes consist of ordinary grades of wrought iron and steel; the starting sheets for the cathodes are of thin sheet iron, previously cleaned of rust and scale."

Other particulars given are: The current efficiency of deposition is very closely 100 percent; "the electromotive force, being one volt, gives about 2.2 lb. (1 kg.) of iron per kilowatt-hour;" the finished cathodes weighed about 20 lb. (9.09 kg.), and the electrolyte can be kept in good working condition with little trouble or expense over a period of at least two months.

The authors state that analyses (which, however, are not given by them) show the purity of the deposited iron to exceed 99.9 percent. "Not a trace of carbon was detected, and silicon, manganese, and other impurities commonly found in iron appear to be

[15] Pfanhauser appears to doubt it. The author can affirm it. For Pfanhauser's comments see *op. cit.*, pp. 613 and 749.

[16] Brit. Assoc. Rep., 1869, p. 67.

[17] Jour. Iron and Steel Inst., 1887 (No. 1), page 71.

[18] Trans. Am. Electrochem. Soc., 1904, **5**, 201. C. F. Burgess and O. P. Watts used $FeSO_4 aq.$ + $NH_4Cl$ (no strength given), a temperature of 20° to 30° C., and a C. D. of about 10 amp./sq. ft. Trans. Am. Electrochem. Soc., 1906, **9**, 232.

absent. The only impurity which has been detected is hydrogen, which is present in appreciable quantities in the metal as taken from the electrolytic tanks. This gaseous element, in its physical or chemical combination with iron, influences, in a most striking manner, the physical properties of the metal. The hydrogen can be driven off almost completely, if not entirely, by heating to a white heat,[19] the evolution commencing at a temperature below 100° C., and becoming rapid at a temperature below a red heat." The metal is hard and brittle, as taken from the tanks; but, after being heated at a welding temperature, assumes properties of malleability and toughness similar to those of Swedish iron.

*Remarks:* Several investigators—Lee,[20] Amberg,[21] and Pfaff[22] (*inter alios*)—have tested the bath of Burgess and Hambuechen, or, perhaps it would be more accurate to say, have tested the conditions adopted by them. The results obtained were, on the whole, favorable; they found the principal defects to be the poor surfaces possessed by the deposits, the surfaces being sometimes pitted and (or) current marked. Pfaff remarks that the deposits adhere well. The present author found that the conditions employed by Burgess and Hambuechen gave good results if the solution was maintained very slightly acid with sulphuric acid, and only then. Deposits up to 0.01 inch (0.025 cm.) thick could be easily obtained in slightly acid solution—deposits that were suitable for "building up" work. In fact, the solution was actually used for that purpose. It was also found that if the temperature was maintained at 60° to 70° C., a current density of 50 amp./sq. ft. (5.50 amp./sq. dm.) could be employed with good results.

The statements (*v. supra*) of Burgess and Hambuechen in regard to the purity of the deposits obtained appear to require qualification. An analysis of iron supplied by Burgess to the Bureau of Standards, Washington, and analyzed by the officials there, showed the following result:

| | C | S | P | Mn | Si | Cu | Total |
|---|---|---|---|---|---|---|---|
| Percent ..... | 0.009 | 0.003 | .... | .... | 0.006 | 0.006 | 0.024 |

[19] *Cf.* J. Cournot, Compt. rend., 1920, **171**, 170, who indicates the difficulty of removing contained hydrogen.

[20] Diss. Dres., 1906.

[21] See below.

[22] Zeit. f. Elektrochemie, 1910, **16**, 220. See also A. Neuburger's comments, Elektrochem. Zeits., 1904-1905 **11**, 77.

And again, the results of two analyses on this iron are given by Schlötter[23] as follows:

| | | S | Si | P | Mn | C | H |
|---|---|---|---|---|---|---|---|
| Sample 1 .. | (Percent) | 0.000 | 0.013 | 0.004 | 0.000 | 0.012 | 0.0072 |
| Sample 2 .. | (Percent) | 0.001 | 0.003 | 0.002 | 0.000 | 0.033 | 0.0083 |

The purity indicated is high, but it is incorrect to say that "not a trace of carbon can be detected."

### (4) *R. Amberg's Method.*[24]

Amberg aimed at producing 1 kg. of pure iron per week. To that end he worked on a 30 liter scale. $FeSO_4$ and an equivalent amount of $(NH_4)_2SO_4$ (or simply the pure double salt), was dissolved in water in such quantity that the solution contained 15 to 45 grams of iron per liter. The best results were obtained from solutions containing upwards of 26 grams of iron (metal) per liter. The surface of the solution was covered with a layer of solid paraffin. Two bars of Krupp's iron, 50 x 50 cm., in cross-section, and wrapped in linen bags, were placed in the center of the trough, and on each side was suspended a cathode sheet (of iron or copper), each having a surface area (facing the anodes) of 600 sq. cm. The solution was sometimes agitated with a glass stirrer. The conditions of three runs are given in the following table:

| No. | Conc. Fe at end of run g./lit. | C.D. amp./sq. dm. | Time hr. | Deposit g. | |
|---|---|---|---|---|---|
| 1 | 45 | 0.2 | 96 | 240 | No stirring |
| 2 | 30 | 0.65 | 72 | 556 | Stirring |
| 3 | 28 | 0.4 | 288 | 1061 | No stirring |

*Note*:—The temperature is not stated. The E. M. F. is given, but no electrode distances.

[23] Galvanostegie, 1. Teil, 1910, 96 (Knapp, Halle).

[24] Zeit. f. Elektrochemie, 1908, **14**, 326, and *ibid.*, 1909, **16**, 125.

The iron content of the deposit, after driving off the hydrogen, was over 99.9 percent.

It is interesting to note Amberg's views: "The production of absolutely pure iron in a liquid is not to be expected, since at the moment of its deposition the deposit can enclose two kinds of substances, namely, (a) particles of electrolyte[25] (this can be reduced to a minimum by taking suitable means), and (b) dissolved (colloidal) impurities from the anode. The most effective means of getting rid of these seems to consist in suspending as anode the product obtained, and re-depositing." Amberg himself employed this method. Others have done so since.

*Remarks:* There does not appear to be much that is really new in Amberg's methods. But his work is of interest in that its specific purpose was to prepare pure iron in considerable quantity for scientific work. It is interesting to compare his methods with those recently adopted by the Bureau of Standards, Washington. (See *post*).

### (5) *A. Pfaff's Solution.*[26]

This author says: "As the result of my researches, I find the following to be the most suitable conditions for the electrolytic separation of iron in thick layers:

2 *N* (at least) ferrous sulphate solution.
0.01 *N* (about) sulphuric acid.
*Current density* (at cathode), 2 amp./sq. dm. (18.5 amp./sq. ft.).
*Temperature,* 70°C.

Pfaff removes the hydrogen bubbles, adhering to the work, by blowing air into the solution; this also agitates the solution.

*Remarks:* Pfaff arrived at the above result after carefully investigating the results of others (Merck[27], Lee[28], Burgess and Hambuechen[29], and some others), and after trying various chemical and mechanical methods for getting rid of hydrogen. His

[25] *Cf.* J. C. W. Humfrey, Carnegie Memoir, 1912, 82.
[26] Zeit. f. Elektrochemie, 1910, **16**, 217.
[27] Zeit. f. Elektrochemie, 1908, **14**, 326.
[28] *Op. cit.*
[29] *Op. cit.*

work, however, does not go beyond the laboratory stage. It is to be noted that Pfaff uses a slightly acidified bath, and makes a point of the importance of this. Many others (including the present author) have found s l i g h t acidity to be very helpful, in the use of sulphate solutions, both in enabling a higher current density to be employed and in helping to keep the solution from readily oxidizing. Further, the temperature mentioned by Pfaff has been found by others[30] to be a very suitable one at which to work. The present author is not, however, at all satisfied as to the advisability of blowing air into such a readily oxidizing solution as ferrous sulphate.

It may be said of Pfaff's work that it was very carefully carried out; and the paper containing his account of it is worthy of careful study.

### (6) *W. A. Macfadyen's Investigations.*[31]

Macfadyen investigated the possibilities of the sulphate solution, both cold and hot, neutral and acid; but he does not appear to have discovered anything essentially new. Summarizing his results, he states: "An aqueous solution of ferrous ammonium sulphate was the electrolyte used, and it was found that whilst excellent results could be obtained from dilute solutions at the normal room temperature, deposition could only be carried out very slowly; with a concentrated solution, however, equally good results were obtained at about seven times the rate usable in the former case.

"Varying acidity of the solution proved to have a great effect on the deposits, and the best results were given by an electrolyte made about 0.005 normal with respect to sulphuric acid.

"By heating the bath to a temperature of 60° C., deposition from a concentrated solution could be satisfactorily carried out at a rate of up to fifty times that which was possible in the case of the dilute cold solution."

Macfadyen's principal numerical results may be tabulated[32] thus:

[30] *e. g.*, E. Merck *(op. cit.)* and H. Lee *(op. cit.)*. And compare the Langbein-Pfanhauser Werke, English patent on Iron Deposition. No. 25,092 (1910).

[31] Trans. Faraday Soc., 1920, **15**, 98.

[32] This tabulation is by the present author, not by Macfadyen.

| | Conc. of $FeSO_4.(NH_4)_2SO_4.7H_2O$ g./lit. | Temp. °C. | Acid $H_2SO_4$ | Maximum C. D. for good deposit amp./sq. ft. |
|---|---|---|---|---|
| 1 | 50-100 | room | | 3.5 |
| 2 | 100-300 | " | | 5 |
| 3 | 315-410 | " | | 16 in small vat<br>24 in 95 lit. vat. |
| 4 | 350 | " | 0.005 *N.* | 23 in 95 lit. vat |
| 5 | 280-420 | 50 | variable | At any temp. from room to 50° C. the numerical maximum C.D. employable is a little greater in value than the numerical value of the temp., using a 60 lit. vat of solution |
| 6[33] | 280-420 | 65 | 0.01 to 0.02 *N.* | 60 to 160 in 60 lit. vat |

*Remarks:* Some points of interest are:

(*a*) The current density stated by Pfaff as the most favorable to use, namely, 19 amp. sq. ft. (2.1 amp./sq. dm.) can, apparently, be much exceeded. But it has to be remembered that the definition of a satisfactory deposit, as the term is used by Macfadyen, may be different from that which Pfaff would give. Macfadyen nowhere defines his term "satisfactory deposit."

(*b*) It is of interest that the numerical value of the C. D. (in amp./sq. ft.) employable varies approximately as the numerical value of the temperature employed, for temperatures up to 50° C., and using acid solutions.

(*c*) Macfadyen found that in respect of concentration a somewhat wide variation could be allowed in all cases.

(*d*) It must be added that the essentially new information given by Macfadyen relates, not to deposition, but to the case-hardening of the deposited iron. This is most interesting and important, and more detailed scientific information upon this subject will be very welcome.

[33] Said to be the best conditions for hot, concentrated acid baths (*Cf.* Pfaff, Hoepfner, and others.)

### (7) *M. Schlötter's Process.*[34]

The particulars of Schlötter's process are as follows:

A solution containing 150 g. of ferrous sulphate and 100 g. of sodium sulphate per liter is treated with sufficient sodium carbonate to neutralize any free acid. The solution is worked at or near boiling point, and a current density of 20 amp./sq. ft. (2.2 amp./sq. dm.) employed.

It is claimed that the deposit contains very little hydrogen and is of great purity, and it is pointed out that lead-lined vats and heating pipes can be used.

*Remarks:* This bath is analogous to the Fischer-Langbein solution. It seems, *prima facie,* to possess all the elements for successful deposition. One possible trouble that might occur in practice is loss from evaporation, which would require a constant water supply to the solution. Even the Fischer-Langbein bath is not free from this defect, though the rate of loss by evaporation is, in that case, slow. A certain difficulty would be caused by separation of salts when the solution was allowed to cool down during week-ends or holidays, and the sulphates would be much more difficult to re-dissolve than are the chlorides. With reference to the temperature suggested, the author is not satisfied that it is necessary (or even advisable) to work at the boiling point. A temperature of 70° to 80° C. is quite sufficient to enable work to be done at a high current density.

## Group II.

### Chloride Solutions.

### (1) *W. M. Hicks' and L. T. O'Shea's Work.*[35]

The solution used by Hicks and O'Shea was 5 percent ferrous chloride with sufficient ammonium chloride added to form the double salt, $FeCl_2.2NH_4Cl$. Their working conditions were:

*Current density* ...0.2 amp./sq. dm., to "strike."
0.15 to 0.18 amp./sq. dm., for continuous deposition.
*E. M. F.* .....about 0.7 volt (electrode distance not given).
*Temperature* .....This is not given; presumably it was ordinary temperature.

[34] D. R. P. No. 309,271, Jan. 12, 1917.

[35] "Some points connected with the preparation of pure iron by electrolysis," The Electrician, 1895, **35**, 843; Brit. Assoc. Rep., 1895, p. 634.

It may be added that "Brunswick black" was used for "stopping off" purposes; anodes of rolled Swedish iron (containing 0.029 S and 0.049 percent C) were used, and they were contained in porous pots. The deposit, which presented a surface of almost silver whiteness and of a somewhat velvety appearance (but was pin-holed), formed at the rate of 3 grams per $dm^2$ in 24 hours, when the apparatus was in good working order.

*Remarks:* Though the object was to obtain pure iron, no analysis of the product is given. It is, however, stated that it was quite free from sulphur.

These authors state that in presence of free acid satisfactory deposits could not be obtained. This is, of course, contrary to the experience of many investigators; and the present author's experience is that it is the quantity of free acid present that is important, and that s l i g h t acidity is not only not a disadvantage, but may, for some purposes, be an advantage in the chloride as in the sulphate bath.

### (2) *E. Merck's Solution.*[36]

Merck states the three conditions he considers necessary for the successful preparation of thick deposits of iron as follows:

(*a*) Agitation of the cathode or the solution,

(*b*) High temperature.

(*c*) Use of ferrous chloride a l o n e .

As an example he gives the following: A solution of 100 kg. of ferrous chloride in 100 kg. of water is filled into an electrolysis vessel provided with either a movable cathode of suitable metal, or a stationary cathode and some mechanical agitation device. The solution is warmed to about 70° C., the agitation commenced, and a current, giving a current density of 3 to 4 amp./sq. dm., passed through the solution.

Pfaff[37] tested the working of this solution. He found (1) that a cohesive deposit could not be obtained from n e u t r a l , d i l u t e , solutions, (2) that if the solution is dilute and a c i d , many outgrowths were formed, (3) that if the solution is c o n - c e n t r a t e d and a c i d , the outgrowths still occur, though

[36] D. R. P., 1900, No. 126,839.

[37] Zeit. f. Elektrochemie, 1910, **16**, 217.

to a less extent, and (4) that if the solution is concentrated and n e u t r a l , the deposit is dense and smooth, but covered with gas pits. Pfaff's general conclusion is that there is no advantage in the use of ferrous chloride over that of the sulphate. This conclusion of Pfaff may be correct so far as concerns the use of the chloride or sulphate alone, but it is certainly incorrect where other salts are added, as, for example, in the case of the Fischer-Langbein bath. (See below).

### (3) *The Fischer-Langbein Solution.*

This solution has been thoroughly tested by the present author,[38] and proved to be one of the best iron-depositing solutions available. Experiments have been made to determine how far the claims made for the bath by its inventors are justified, and the disadvantages as well as the advantages attaching to the use of the bath.

The principal Fischer-Langbein patents[39] only will be considered. The electrolyte given in the specification of the 1908 patent is as follows:

| | |
|---|---|
| 450 grams ..... | $FeCl_2$ *aq.* |
| 500 grams ..... | $CaCl_2$ |
| 750 c.c. ..... | Water |

*The temperature* must not be less than 90° C. The working temperature is given as 110° C.

*The current density* at which to work is given as "up to 20 amp./sq. dm.

It is claimed that:

(*a*) The addition of a hygroscopic salt, *e. g.*, $CaCl_2$, $AlCl_3$, prevents alteration of the electrolyte at higher temperatures, whether by evaporation or oxidation.

(*b*) A high current density is usable with such a solution as those proposed.

The 1909 patent states that it is found that certain chlorides which are not themselves hygroscopic, *e. g.*, sodium chloride, unite with ferrous chloride to give hygroscopic double chlorides.

[38] The results will be found embodied in a separate communication.

[39] List of patent specifications relating to the above chloride bath; D. R. P., 1908, No. 212,994; D. R. P., 1909, No. 228,893; D. R. P., 1910, No. 230,876; English patent No. 25,092 (1910).

Thus sodium chloride and ferrous chloride give $NaFeCl_3$, which is hygroscopic. Hence such salts can replace the calcium or other chloride of the 1908 patent.

The 1910 patent applies the use of hygroscopic electrolytes to the refining of iron. An analysis of iron deposited from the Fischer-Langbein bath is given as follows:

| | Percent |
|---|---|
| Fe | 99.986 |
| S | under 0.008 |
| P | 0.007 |

Cu, C, Mn, and Si are all absent.

It is mentioned in this specification that a temperature between 60° and 80° C., can be used instead of the higher ones (above 90° C.) which the other specifications state to be necessary.

W. Pfanhauser, Jr.,[40] gives an analysis[41] of iron produced by the above process. It reads:

| | Percent |
|---|---|
| Fe | 99.99 |
| S | 0.007 |
| P | 0.004 |

Cu, C, Mn, Si all absent.

Pfanhauser maintains that the iron produced by this process has the highest purity yet reached. He claims that it is purer than the iron produced by Merck's method; and he points out, further, that Merck's bath suffers from the disadvantage that a very large amount of water is used up which has continually to be replaced during work.

## Group III.

### Sulphate-Chloride Solutions.

### (1) *F. Varrentrapp's Solution.*[42]

This investigator recommends a solution composed thus:

| | |
|---|---|
| 4 lb. | Ferrous sulphate |
| 3 lb. | Sal ammoniac |
| 30 lb. | Water |

He states that this was a solution that proved itself valuable in practice. The sal ammoniac can be omitted, but the bath works

[40] Galvanotechnik, 1910, 750.

[41] The Analysis was made by Dr. Kröhnke, Berlin.

[42] "Galvanische Fällung von Eisen in cohärenter Form." Ding. Polytech. Jour. 1868, 187, 152.

faster if it contains that salt. No deposition conditions are given by Varrentrapp, but of the deposit it is said, that it has a light color, and that a thickness of 2 mm. could be obtained in 14 days. "The deposited iron, well washed and dried by warming, resists rust well; thrown into concentrated HCl, a few bubbles were evolved only after a long time. In the cold a thin plate is not eaten through by great excess even in 24 hours. Cold dilute HCl behaves likewise; but on heating a brisk evolution of hydrogen occurs, which ceases as soon as the reagent glass is removed from the lamp, and the solution then continues slowly till all the iron is dissolved."

### (2) *C. F. Burgess' Bath.*

Burgess mentions[43] a solution (similar to that of Varrentrapp) as being in use for iron refining at the University of Wisconsin. "Using an electrolyte containing 40 grams of iron per liter in the form of ferrous sulphate together with 40 grams of ammonium chloride, it has been found possible to conduct a continuous refining operation for many months at a current density of 6 to 10 amp./sq. ft. (0.66 to 1.1 amp./sq. dm.) of cathode surface, and at a potential difference of about one volt. The current efficiency is very close to 100 per cent." The same author states (*op. cit.* p. 182): "We have found that electrolytic iron can be produced with a purity as high as 99.97 percent or perhaps even better, using extraordinary precautions."

### (3) *O. P. Watts' and L. H. Li's Sulphate-Chloride Solution.*[44]

The solution used by Watts and Li had the following composition:

| | |
|---|---|
| $FeSO_4.7H_2O$ | 150 g. |
| $FeCl_2.4H_2O$ | 75 g. |
| $(NH_4)_2SO_4$ | 120 g. |

per liter solution.

To this were added from 6 to 10 g. of ammonium oxalate. Excellent deposits were said to be obtained in this solution in runs that lasted 10 days or more, working at 10 amp./sq. ft. (1.1 amp./sq. dm.). The solution had a specific gravity of 1.125 at 20° C., and was worked at ordinary temperature.

[43] "Electrolytic Refining as a Step in the Production of Steel." Trans. Am. Electrochem. Soc., 1911, **19**, 181.

[44] Trans. Am. Electrochem. Soc., 1914, **25**, 529

The object of the research was to find some "addition agent" that, when added to the depositing solution, would enable a thicker deposit, having a smooth and even surface, to be obtained from it. The "addition agents" (other than ammonium oxalate) that were tried included: hexamethylenetetramine, phenol, formalin, dextrin and resorcin. Each of the first three appear to have given good results, but the oxalate was preferred to them. It is not very clear whether the bath was acid or neutral; but some results are given showing that excellent results were obtained from baths that are definitely stated to contain no acid. It is, therefore, to be presumed that acid was not considered necessary.

*Remarks:* It must be said that, though carefully following the instructions given in the paper, the present author could not obtain results similar to those claimed by Watts and Li. One difficulty experienced was to get a n d k e e p the oxalate in solution. Some yellow precipitate (double oxalate of iron and ammonia) was always thrown out of solution,[45] and more was precipitated as electrolysis proceeded.

On the use of oxalate in baths for iron deposition R. Amberg remarks: "The addition of oxalate can today be shown to be useless."[46] At the same time it must be added that the successful results claimed by A. Neuburger and N. von Klobukow (in 1890) were obtained in a solution in which the excess of ammonia was neutralized by oxalic acid.[47]

In regard to the use of "addition agents" in solutions for iron deposition the following suggestions are advanced:

(*a*) A review of the literature shows the addition of all such substances as those proposed by Watts and Li to be quite unnecessary.

(*b*) That such substances ought not to be used unless their employment is essential to the success of the deposition process. This statement is based upon the following reasons: Nothing

[45] *Cf.* A. Classen, Quantitative Analysis by Electrolysis (Hall's Translation), 1913. 147 *et seq.* (Wiley, New York) and A. Classen and Reis, Ber., 1881, **14**, 1622.

[46] Zeit. f. Elektrochemie, 1908, **14**, 327. This statement of Amberg is not applicable to the use of ammonium oxalate in quantitative electro-analysis.

[47] Elektrochem. Zeits., 1904-1905, **11**, 77. Their solution, which, however, was not thoroughly investigated, was made as follows: Sulphate of iron (crystals) was dissolved in water (no quantity is given), the solution carefully neutralized with ammonia, and any excess of this was taken up by oxalic acid. This acid was also used to dissolve the "iron carbonate" that frequently separated during electrolysis. The C. D. employed was 1 amp./sq. dm. No temperature is given.

at all is known as to how such addition agents as those proposed (those of the organic type) cause the change, for better or worse, in the deposit that they undoubtedly do effect. When, therefore, such substances are added to a solution, scientific control of its working is to a great extent lost, and to that extent resort must be made to "rule of thumb" methods. Results obtained by such methods are unsatisfactory; they are uncertain, and no reliance can be placed in the operation of an uncontrolled process.

(c) That the work of Watts and Li upon the effects of adding organic substances to solutions for depositing iron has called attention once more to the necessity for wide and deep scientific research in matters pertaining to the electrodeposition of metals.

## General Researches.

### (1) *Alexander Watt.*[48]

The experimental work of Mr. Watt is of great interest and importance, both historically and practically. He investigated solutions of a large number of iron salts, both organic and inorganic, and also several solutions of mixed electrolytes. Further, his work extended to both ferrous and ferric salts. The phenomena observed and the characters of the deposits obtained are stated in very considerable detail in the numbers of the "Electrician" mentioned in the foot-note.

Mr. Watt does not appear to have had in mind the formation of thick deposits; his aims were scientific rather than practical. But as regards the application of iron solutions to practical purposes, he says: "If we consider the practical application of iron solutions in the electrodeposition of that metal upon other metallic surfaces, as in the so-called steel-facing of engraved copper plates, for example, I am disposed to give the preference to the following salts for making up iron baths, and if these are prepared with care, and from good materials, there should be no difficulty in obtaining good results from either of them. (1) Ammonio-sulphate of iron. (2) Sulphates of iron and magnesia. (3) Sulphate of iron and chloride of ammonia. (4) Sulphate of iron *per se*. To prevent the solutions from becoming oxidized many different substances have been added to iron baths, as glucose

[48] The Electrician, Nov. 11 and 25, Dec. 16 and 30, 1887, and Jan. 13, 1888.

(grape sugar), glycerine, etc., but I am disposed to think, from experiments I made in this direction, that small doses of citric or tartaric acid will be found more effectual, while these vegetable acids have also a tendency to improve the brightness of the iron deposit."

*Remark:* It is to be regretted that Watt's work is not better known. It forms an excellent starting point for research on iron deposition; and a wider knowledge of it would have saved later investigators much time and trouble, even though it would, at the same time, have deprived some of them of their "discoveries."

Watt investigated solutions of the following salts:

(*a*) *Inorganic Single Salts.*

Ferrous chloride
Ferric chloride
Iodide of iron
Ferrous nitrate
Ferric nitrate
Phosphate of iron
Perphosphate of iron
Ferrous sulphate
Ferric sulphate
Ferric ammonium sulphate
Ferrous and magnesium chloride
Ferrous and sodium chlorides
Ferrous ammonium nitrate
Ferrous nitrate and potassium nitrate
Ferrous ammonium sulphate
Ferric potassium sulphate
Persulphate of iron and ammonia
Persulphate of iron and sodium
Persulphate of iron and potassium
Potassium ferrate
Ferrous sulphate and ammonium chloride

(*b*) *Organic Salts.*

Ferrous acetate
Ferric acetate
Ferrous benzoate
Ferric benzoate
Citrate of iron
Ferric citrate
Cyanides of iron
Ferrocyanide of iron
Iron gallate
Iron lactate
Perlactate of iron
Oxalate of iron
Ferric oxalate
Salicylate of iron
Iron tannate
Tartrate of iron
Pertartrate of iron
Ferric acetate and sodium acetate
Ferrous ammonium citrate
Iron potassium oxalate
Iron potassium tartrate
Soluble Prussian blue

Watt gives detailed particulars of the phenomena in each case, and he describes the deposit where one was formed. He also appears to have tested Klein's bath.

(2) *J. Thiele.*[49]

Thiele's object was to prepare iron as free as possible from sulphur. His final method was as follows: 200 g. of anhydrous

[49] Zum. Nachweis des Arsens. Lieb. Ann., 1891, **265**, 58.

ferrous chloride (commercial) were dissolved in 500 c.c. of water. This solution was digested with the purest obtainable iron to throw down more "negative" metals, and then treated with barium chloride to precipitate any sulphate. The filtered solution was then mixed with 25 c.c. of glacial acetic acid, and the mixed solutions electrolyzed.

"The iron so obtained is easily separable from the platinum sheet" (the cathode), "its inner surface has a metallic luster; its outer surface is black and gives a black powder which becomes iron-grey on heating to redness in a current of hydrogen. It is very brittle, breaks in pieces, and oxidizes quickly. It must, therefore, be quickly rinsed with water, alcohol, and ether, and dried in vacuo over sulphuric acid. It is best kept in a desiccator. The iron so produced still contains a small amount of enclosed water, even after standing for weeks in the desiccator. The metal is dissolved by acid with extraordinary rapidity a n d w i t h o u t a n y residue; hydrogen is evolved even on boiling" (the metal) "in water." Upon close analysis, Thiele found his iron to contain 0.0048 to 0.0075 percent of sulphur.

*Comment:* The fact that Thiele found is so difficult to obtain the pure iron he required for analytical work is worthy of emphasis. The matter will not be pursued here, as the purity of electrodeposited iron will be dealt with fully elsewhere, [50] but a remark of Bertram Blount may be quoted: " . . . the preparation of pure iron electrolytically is as difficult as it is by purely chemical means, and this, as every chemist knows, is one of the most exacting tasks to which he can set himself." [51]

### (3) *H. Lee.*[52]

Lee's work, which formed the subject matter of a Dissertation (Dresden, 1906), was published as a section of F. Foerster's "Beiträge zur Kenntnis des elektro-chemischem Verhaltens des Eisens." The great value of Lee's work consists in the careful examination made of the purity of iron deposited from a number of proposed solutions (Klein's, Hicks and O'Shea's, and others), and the effects of the various impurities found in the metal upon

[50] This subject will be considered in a separate communication.

[51] "Practical Electrochemistry," 1906, p. 282 (Constable, and The MacMillan Co., New York).

[52] Abhandl. der Deutsch, Bunsen Gesellschaft, Nr. 2, 1909, pp. 59 to 83.

its properties. These are matters of great importance both in the electro-refining process and also in the electrolytic preparation of iron for use in research work on the properties of that metal. The only part of Lee's paper that is of immediate importance to this paper is Section A; in this section are included the results obtained upon testing a number of solutions proposed for the deposition of iron. Lee's criticisms upon the solutions he tested are valuable, and should be considered carefully by anyone who is setting out to deposit iron.

### (4) *A. Russ and A. Bogomolny.*[53]

These investigators, commenting upon their tests of the solutions given by Burgess and Hambuechen,[54] Hiorn,[55] Langbein,[56] and Pfanhauser,[57] say that they found them unsatisfactory in that they were unable to obtain from them deposits that were homogeneous and of considerable thickness. They investigated, *de novo,* both sulphate and chloride solutions, and obtained good results from the following baths:

#### (*a*) *Sulphate Solution.*

70 g.....$(NH_4)_2Fe(SO_4)_2$, crystals.
1 lit.....water.
*Temperature*.....ordinary (higher temperatures lead to inferior deposits)
*C. D.*.....0.5 amp./sq. dm.

The maximum thickness obtainable from this solution was 1.2 mm.

#### (*b*) *Chloride Solution.*

1 kg.....$FeCl_2$.
1 lit.....water.
*Temperature*.....60° to 70° C.
*C. D.*.....0.4 amp./sq. dm.

The maximum thickness obtainable was, in this case, 0.3 mm.

*Note:* The maximum thickness obtainable refers to a smooth, non-porous deposit.

In the cases of both solutions they lay stress upon the fact that it is preferable to raise the current density g r a d u a l l y to the maximum, and upon the importance of cathode movement.

[53] Zeit. f. Elektrochemie, 1906, **12**, 697.
[54] *Ante,* p.
[55] Eng. Pat. No. 4660 (1895). The present author can assert from experience that Hiorn's solution is of no use in practice, except, perhaps, in steel facing work, for which, indeed, it was designed.
[56] Handb. der Elektrolytischen Metallniederschläge, pp. 425 to 427 and 580 to 584.
[57] Elektroplattierung, pp. 583 and 584.

Russ and Bogomolny investigated also the results obtained after the addition of various substances,[58] other than iron salts, to the solutions; and they say that in no case was a deposit improved by such addition.

The experimental results obtained by Russ and Bogomolny when working on Klein's solution are interesting; they fully confirm those obtained by most other workers.

Russ and Bogomolny, in investigating Klein's bath,[59] followed the instructions of Maximowitsch (*v. sup.*), proceeding as follows: "A 2-lit. vessel was filled with a solution made of 200 g. $FeCl_2$ (Merck) or $(NH_4)_2Fe(SO_4)_2$, 50 g. $MgSO_4$, and 1 lit. water. 8 g. of $NaHCO_3$ were added, the addition causing a dirty scum to form on the surface. The solution, at first cloudy, gradually cleared, with the formation of a voluminous precipitate. Twice weekly, during the continuance of the electrolysis, $NaHCO_3$ was added to the bath in portions of 8 to 10 g. The anode consisted of sheet iron; the cathode, which was bent to the common cylindrical form, was de-greased with concentrated KOH, and rotated by a motor. The current density amounted to 0.3 amp./sq. dm., and the E. M. F. to 0.6 to 0.7 volt.[60] An experiment lasted three weeks.

"The deposited iron was at first not very bright (*wenig glänzend*), but it was quite evenly distributed. After 4 days some individual pores appeared on both the upper and lower parts of the deposit, but these disappeared again later. The current efficiency was about 96 percent. The layer" (of deposit) "on the cathode had a thickness of 2 mm. and had not become non-homogeneous."

Russ and Bogomolny conclude: "An addition of $MgSO_4$ and $NaHCO_3$ to iron ammonium sulphate and ferrous chloride solutions makes it possible to obtain a deposit of (so far as their experiments went) any thickness and without pores and hollows." They found that neither $MgSO_4$ nor $NaHCO_3$, alone, produced the favorable results obtained by the co-addition of these substances.

[58] *e. g.* alcohol, glycerin, aldelyde, organic acids, tartrates, acetates, oxalates, sugar, etc.

[59] *Op. cit.* at p. 701.

[60] No electrode distance is given.

*Remark:* It will be noticed that Russ and Bogomolny obtained equally good results whether the iron salt employed was the double sulphate or the chloride. It thus appears that the iron salt employed in Klein's solution can be the single sulphate, the double sulphate, or the (ferrous) chloride.

### (5) *S. Cowper-Coles' Solution and Process.*[61]

"The electrolyte employed consists of a 20 percent solution of sulpho-cresylic acid saturated with iron. Sulpho-cresylic acid is a cresol-sulphonic acid containing approximately 108 parts of cresol and 98 parts of sulphuric acid. The cresol contains: ortho, 35, meta, 40, and para, 25 percent. This cresol is heated with sulphuric acid, yielding isomeric cresol-sulphonic acids.[62]

"In some cases it is advantageous to add small quantities of carbon disulphide, the temperature of the solution being about 70° C., the current density about 100 amp./sq. ft. (11.1 amp./sq. dm.). The solution is kept charged with iron oxide, which is kept in suspension in the electrolyte by means of stirrers, by moving one or both of the electrodes, or by circulating by means of a bucket pump. The specific gravity of the electrolyte having the iron oxide in suspension is about 1.32."

Cowper-Coles seems to have also used a chloride solution, but no particulars of this are given in the paper. (*v.* Palmaer and Brinell, *infra.*)

The solution was used for the production of finished iron sheets and tubes (deposited on a rotating mandril) in one operation.

*Remarks:* Neither the bath nor the process as a whole (as described in Cowper-Coles' paper) commends itself to the present author, because it is not clear from the chemistry given what was the constitution of the electrolyte, nor how it was made.

A bath charged with iron oxide is not to be recommended if "finished" articles are to be produced. The structure of the deposit can scarcely be satisfactory, since it is difficult to conceive that oxide would not be included in it.

Cowper-Coles states (*op. cit.*, p. 145) that: "Electrolytic steel, with considerable variation in the percentage of carbon, can also

[61] Jour. Iron and Steel Inst., 1908 (No. 3), 134; and *v.* Elektroch. Zeits., 1908-1909, **15**, 254 and 277; and Met. and Chem. Eng., 1913, **11**, 197.

[62] It may be mentioned that a similar solution for zinc deposition was patented in the United States. See U. S. Patent No. 905,837 (1908).

be produced." It would be interesting to know what he means by "steel." It is quite conceivable that, from a solution of the type given, a deposit containing a variable amount of carbon could and would be produced, and it is more than probable that the content of carbon would be uncontrollable. Indeed, it is not easy to believe that a deposit free from carbon could be produced from such a solution.[63] But it is suggested that a deposit of iron containing carbon and a deposit of steel (as ordinarily understood by a metallurgist) are two very different things.

The working of such a solution as that proposed by Cowper-Coles would be very difficult to control. The reactions occurring at the anode (or, even at the cathode) would be unknown, since the mechanism of the electrolysis of cresol-sulphonic acid, whether ortho, meta, or para, has not been worked out.

Cowper-Coles himself does not appear to have continued the use of the bath he describes. He would seem to have resorted to the use of the chloride, as is shown in the following report:

W. Palmaer and J. A. Brinell,[64] who specially investigated the process on behalf of the Swedish Ironmasters Association, describe it as "an electrolytic refining process," in which iron sheets and tubes of nearly pure iron are produced from pig iron. The electrolyte used, they say, was a saturated ferrous chloride solution, containing also iron salts of certain organic acids and an amount of iron oxide is added so that the solution has the consistency of gruel. The conditions of deposition that obtained on two occasions when they were present were as follows:

| | Electrolysis I. | Electrolysis II. |
|---|---|---|
| Time of run | 2 hrs. 2.5 min. | 2 hrs. 30 min. |
| C. D. (cathode) average | 6.74 amp./sq. dm. | 6.91 amp./sq. dm. |
| E. M. F., average | 1.34 volts (1.25-1.45)[65]. | 1.43 volts |
| Temp., average | 92° C. (88°-94°). | 94.5°C. |
| Peripheral speed | 120 m./min. | 125 m./min. |
| Efficiency (cathode) | 83.5 percent. | Owing to the sheet being brittle, and breaking up, some pieces were lost. Hence, the efficiency was not determinable with accuracy. |

(The efficiency value is based upon the assumption that 1 ampere will deposit 0.0174 g.Fe per min. from the solution of ferrous salts, there being no appreciable amount of ferric salts present).

[63] *Cf.* R. Kremann and his co-workers.

[64] Met. and Chem. Eng., 1913, **11**, 197. This article contains very full details on (1) the preparation of the solution, (2) analyses and mechanical tests of the product, and (3) economic considerations.

[65] The distance between the electrodes was apparently 40 mm. See *op. cit.*, p. 198.

The opinion of Palmaer and Brinell, based upon their investigations, was as follows:

(*a*) *As to the life of the electrolyte.*

"From the short investigation we made it is too precarious to draw any conclusions in regard to the life of the electrolyte."

(*b*) *As to the process in general.*

A careful reading of the paper of Palmaer and Brinell leaves the impression that they regard the process as insufficiently tried and as being (then) in the experimental stage.

(*c*) *As to the purity of the deposit.*

"It might be expected that nearly pure iron would be deposited—that is, soft sheet iron without carbon or impurities. There is, however, in fact, some carbon in the iron obtained by the Cowper-Coles process, and there are also traces of phosphorus and sulphur" (*op. cit.*, p. 198).[66] As regards the hydrogen and chlorine found, on analysis, to be present, it is said: "The percentage of hydrogen is remarkably high in the non-heated sheet" (p. 201); and "the high percentage of chlorine is very remarkable, and if it cannot be avoided is very disadvantageous." The presence of the hydrogen is attributed to the high current density employed, and that of the chlorine to the possibility of insufficient washing of the sheet before heating and the consequent retention in the pores of the metal of some of the electrolyte, namely, ferrous chloride.

W. Palmaer gives some additional particulars of the properties in a communication to the Svenska Teknologforeningen, Sweden.[67] He states here that in mechanical and magnetic properties the iron deposited from Cowper-Coles' bath compares favorably with sheet (Martinbloch) from the Avesta Works; but he says that it rusts badly, probably in consequence of the high (0.02 percent) chlorine content.

L. Guillet[68] dismisses the process somewhat summarily, saying: "This process, which was analogous to the Elmore process for making copper tubes, has not yielded results of much importance."[69]

[66] The author's analyses, conducted at the Materials Testing Laboratories, Stockholm, show Si, Mn, H, and Cl, to be present.

[67] Jan. 16, 1913. Abstracted in Chem. Ztg., 1913, **37**, 393.

[68] Jour. Iron and Steel Inst., 1914 (No. 2), p. 67.

[69] But see Cowper-Coles reply, *op. cit.*, p. 81.

### (6) *E. F. Kern.*[70]

Dr. Kern concerned himself with the "Electrolytic Refining of Iron," that is to say, with the continuous deposition of (thick) deposits of pure iron. He worked with four types of solution, namely:

(*a*) *The Fluosilicate.* This proved very unsatisfactory, and is, therefore, not further noticed here.

(*b*) *A Ferrous sulphate solution.* This contained 40 grams $FeSO_4$ $7H_2O$ per 100 c. c., giving an electrolyte with about 8 grams of Fe (metal) per 100 c. c.

(*c*) *A Ferrous-sodium sulphate solution.* This contained 30 grams of ferrous sulphate (crystals) and 21 grams of Glauber's salt per 100 c. c., giving a solution containing about 6 of Fe (metal) and 3 percent of Na.

(*d*) *A Ferrous-sodium chloride solution.* This consisted of 28.5 grams of $FeCl_2$ $4H_2O$ and 10.2 grams of NaCl per 100 c. c., which gave an iron content of 8 and a sodium content of 4 percent. One cubic centimeter of concentrated HCl was added per 100 c. c. of electrolyte, in order to "clear" the solution.

Dr. Kern has so clearly summarized the results of his researches that they are given here in his own words. He states his conclusions thus (*op. cit.*, p. 118):

"Neutral ferrous fluosilicate electrolytes are not suitable for electrolytic refining of iron, as they are slowly decomposed with the separation of silica, which settles to the bottom of the cell and also collects on the anodes and cathodes. The deposits from ferrous fluosilicate electrolytes are smooth and solid, of dull gray color and very brittle, due to the contained silica. The E. M. F. required for electrolysis of ferrous fluosilicate electrolytes with a C. D. of 10 to 20 amp./sq. ft. (1.1 to 2.2 amp./sq. dm.) was 0.9 to 1.2 volts, when the temperature was 20° C., and 0.55 to 0.7 volts, when the temperature was 60° C.

"Good deposits of iron were obtained by the electrolysis of neutral electrolytes containing either 8 percent of iron as $FeSO_4$, or 6 Fe and 3 percent Na as sulphates, or 8 Fe and 4 percent Na as chlorides. The E. M. F. required for electrolysis of neutral

[70] Trans. Am. Electrochem. Soc., 1908, 13, 103.

$FeSO_4$ electrolytes containing 8 percent Fe with a C. D. of 10 to 20 amp./sq. ft. was 1.15 to 1.4 volts, when the temperature was about 20° C., and 0.8 to 0.98 volts when the temperature was about 50° C.

"The E. M. F. required for electrolysis of neutral sulphate electrolytes containing about 6 Fe and 3 percent Na with a C. D. of 10 to 20 amp./sq. ft. was 0.95 to 1.2 volts, when the temperature was about 20° C., and 0.5 to 0.85 volts, when the temperature was about 50° C.

"The E. M. F. required for the electrolysis of neutral chloride electrolyte containing about 8 Fe and 4 percent Na, with a C. D. of 10 to 20 amp./sq. ft., was 0.6 to 0.8 volts, when the temperature was about 20° C., and 0.4 to 0.5 volts, when the temperature was about 50° C.

"On starting the electrolysis of sulphate and chloride electrolytes, the deposits of iron peeled from the cathode and curled, due to the presence of ferric salts in the solution. After the solutions were electrolyzed for about 3 hours the deposits formed smooth, solid and adherent.

"Boiling the solutions previous to electrolysis liberated the dissolved gases and caused the deposits to form less pitted.[71]

"The deposits of iron formed smoother when the electrolysis was conducted at 40° to 60° C. than when conducted at normal temperature.

"The deposits formed in the neutral chloride electrolytes, containing iron and sodium chlorides, were finer grained and more flexible than those formed in neutral sulphate electrolytes.

"The deposits of iron formed in neutral sulphate or chloride electrolytes, containing no ammonium salts, became quite malleable when they were heated above redness. The deposits from the chloride electrolytes, being finer grained, were the most ductile, and could be hammered double after being heated.

"The deposits of iron from electrolytes containing ammonium salts were harder, more brittle and also less rapidly oxidized than those from electrolytes which contained no ammonium salts. This suggested the possibility that iron formed in neutral ferrous

[71] C. F. Burgess and O. P. Watts also boiled their solutions to expel dissolved gases, which they also believe to be a cause of "pitting." Trans. Am. Electrochem. Soc., 1906, 9, 232.

ammonium electrolytes contained either a nitride or an ammonium compound of iron.

"When the electrolytes are not protected from the atmosphere, it is necessary to occasionally add a few drops of acid in order to clear the solution by dissolving the resulting basic salts."

*Remarks:* The experiments were conducted on quite a small scale, even as laboratory experiments, being often carried out in 650 c. c. of solution contained in glass beakers. All who have had much to do with electro-deposition know well that results obtained from such small scale work can only be regarded as indicative. Results obtained from small scale work are not necessarily producible in the workshop; modifications may be necessary in the conditions of deposition, in order to obtain success. Further, as Professor Burgess remarked (in the discussion on Kern's paper) "conclusions as to the quality of the deposit cannot be made in a few hours, or even in a few days." The above remarks are not made in disparagement of Dr. Kern's work; they are made in the hope of guiding those who are less experienced in the electrodeposition of metals than is Dr. Kern. The chief merit of his work is, in the present author's opinion, that he gives concise and fairly complete details, such as will enable anyone to try for himself whether any one or more of the solutions proposed is of use for this or that particular object.

A point of difference between Dr. Kern's experience and that of the present author is worthy of remark. It relates to the properties of the deposited iron. Dr. Kern finds that deposits from the neutral double chloride bath are "finer grained and more flexible" than deposits from neutral sulphate solutions. The present author has continually found that the finer the grain of the deposited iron, in whatever solution it is formed, the l e s s flexible and more brittle that deposit is; and that deposits formed in chloride solutions are not of finer grain than those formed in sulphate solutions, where like conditions of deposition have obtained in the two cases. In making the foregoing remarks the present author has no intention of disputing the accuracy of Dr. Kern's observations; the intention is to call attention to a difference of experience which would most probably be removed by further research.

## (7) *A. Müller.*[72]

Müller's work is concerned with both the deposition of iron and the properties of the deposited metal. Only the deposition part will be considered here. His objects were: (i) The production of a material of the purest quality—free from silicon, phosphorus, sulphur, manganese and carbon; and (ii) the production of a large quantity of such iron in the shortest possible time.

With reference to the work of Burgess and Hambuechen, Müller says that, since these authors give no information as to the concentration of their solution, he used baths containing 15, 30 and 50 percent $(NH_4)_2\,Fe(SO_4)_2.aq.$, and found, working under the conditions given below in Runs 1 and 3, that 30 and 50 percent solutions gave the same results.

It will be convenient to consider Müller's work in separate sections, having reference to (*a*) Purity of deposit, (*b*) Influence of current density, (*c*) Influence of concentration, and (*d*) Influence of temperature. A comparison of the sulphate and chloride baths is maintained throughout.

### (*a*) *Purity of Deposit.* (i) *Sulphate solution.*

| No. | Analysis | anode percent | deposit percent | Experimental conditions and results |
|---|---|---|---|---|
| 1 | Si | 0.008 | 0.0079 | Electrolyte $(NH_4)_2Fe(SO_4)_2.6H_2O$ |
| | P | 0.026 | 0.0042 | |
| | S | 0.025 | 0.0099 | C. D. .....0.28 amp./sq. dm. |
| | Mn | 0.056 | 0.0100 | E. M. F. .....1 volt. |
| | C | 0.071 | 0.0720 | Time .....200 hr. |
| | | | | Deposit .....825 g. |
| | Total impurity | 0.186 | 0.1040 | Efficiency .....98 percent |
| 3 | Si | 0.002 | 0.0070 | Electrolyte (as in 1) |
| | P | 0.037 | 0.0058 | |
| | S | 0.002 | 0.0078 | C. D. .....0.4 amp./sq. dm. |
| | Mn | 0.019 | 0.0039 | E. M. F. .....1 volt. |
| | C | 0.035 | 0.0690 | Time .....168 hr. |
| | 'Schlacke' | 0.4 | . . . | Deposit .....825 g. |
| | | | | Efficiency .....94 percent |
| | Total impurity | 0.495 | 0.0935 | |

[72] Metallurgie, 1909, 6, 145.

The results contained in the above Tables 1 and 3 are typical. Müller remarks that, in his opinion, the analyses show that the sulphate solution is of no use where deposits containing the minimum of sulphur are required. As Table 3 shows the sulphur content of the deposit may be higher than that of the anode. He, therefore, tried chloride baths and obtained results of which those contained in Run 7 are typical.

(ii) *Chloride solution.*

| Run No. | Analysis | | | Experimental conditions and results |
|---|---|---|---|---|
| | | anode percent | deposit percent | |
| 7 | Si | 0.008 | 0.0053 | Electrolyte $FeCl_2$ |
| | P | 0.026 | 0.0045 | |
| | S | 0.025 | 0.0024 | C. D. .....0.52 amp./sq. dm. |
| | Mn | 0.056 | 0.0090 | E. M. F. .....1 volt. |
| | C | 0.071 | 0.0630 | Time .....336 hr. |
| | | | | Deposit .....1840 g. |
| | Total impurity | 0.186 | 0.0842 | Efficiency .....91 percent |

Comparing Runs 1 and 7, Müller points out that the sulphur has fallen considerably, about 75 percent, and that carbon and silicon have, together, fallen 15 percent.

(*b*) *Influence of Current Density.* (i) *Sulphate solution:* The best current density was found to be 0.3 to 0.8 amp./sq. dm. With Burgess and Hambuechen's process, at ordinary temperature, 0.8 amp./sq. dm. could be used; but with Maximowitsch's solution only 0.5 amp./sq. dm. was permissible. It was found that the higher the current density was, the more pitted and less serviceable the deposits became. The deposits were, usually, thicker at the edges than in the middle.

(ii) *Chloride solution:* The best current density was found to be 0.7 amp./sq. dm.; higher current densities caused the deposits to be thinner and less homogeneous.

(*c*) *Influence of Concentration.* (i) *Sulphate solution:* Thirty percent concentration was found to give the best results towards the attainment of the author's purpose. Fifty percent solutions gave no better results than the 30 percent.

(ii) *Chloride solution:* "For chloride baths the more concentrated solutions have shown themselves to be the best. Baths of less concentration than 30 percent resulted in split and stripped deposits. The edges of the strips were bent towards the anode, as Haber has already observed (Zeit. f. Elektrochemie, 1898, **4**, 410), a circumstance to which the brittleness of the electrolytic iron contributes. Baths of greater concentration give rise to a blister surface, and the oval holes also increase in number with the concentration."

(*d*) *Influence of Temperature.* (i) *Sulphate solution:* Müller agrees with Russ and Bogomolny[73] that room temperature is preferable to a higher one.

(ii) *Chloride solution:* Müller states that he prefers to use the chloride baths also at the ordinary temperature.[74] Referring to some experiments with Merck's solution, he says (*op. cit.*, p. 149): "The electrolytic iron produced according to D. R. P. Merck at 70° C. was 9.6 mm. thick, but of this only 0.7 mm. was homogeneous, the remaining layer had pores and long outgrowths—which were caused by the too great evolution of gas—and oxidized at once in the air."

*Comments:* Müller evidently considers the chloride bath preferable to the sulphate for the production of pure iron. The present author is, however, not satisfied that Müller has proved it to be so. Palmaer and Brinell[75], Humfrey,[76] and others, have noted the inclusion of electrolyte in the deposits from the chloride bath; and the author can confirm these observations. Yet Müller says nothing in his analyses of chlorine being present in the deposits. It may, however, be that a deposit formed at a low current density (low, that is, relatively to the high densities that can be used with the chloride bath) is less likely to contain hollows in which electrolyte can be enclosed than is one deposited at a high current density, as was the iron referred to by Palmaer and Brinell, and Humfrey, and as was that examined by the present author. This seems to be possible in view of Müller's observation that when a

[73] Zeit. f. Elektrochemie, 1906, **12**, 697. But *cf.* A. Pfaff, and others.

[74] *cf.* Russ and Bogomolny, who give 60° to 70° C. as the best temperature at which to work the chloride bath.

[75] *v. Ante,* p.

[76] Carnegie Scholarship Memoir, 1912, 4, 82.

high current density was employed by him, he found that the deposit rusted quickly.

With respect to his observations on the effect of temperature, Müller does not record any experiments made with the Fischer-Langbein bath. It may be that if he had been familiar with the working of this solution, his views as to the temperature at which the chloride bath can be successfully worked, would have been different. Even remembering Müller's principal object, namely, the production of the purest obtainable iron, still it is the present author's opinion that the chloride solution is at least the equal of the sulphate. So far as analyses prove anything, those given by the No. 230876 (1910) patent and by Pfanhauser[77] indicate a purity that has not been exceeded (or even equalled) by deposits from the sulphate solution. Microscopic observation has convinced the author that the purity of the deposits from the Fischer-Langbein bath can be very high, when the proper conditions of working the solution are observed. It is only when this has not been the case that oxide and liquid inclusions are contained in the deposits.

### (8) *J. R. Cain, E. Schramm, and H. E. Cleaves.*[78]

This work, carried out at the Bureau of Standards, Washington, is concerned with the preparation of really pure iron for the purpose of determining the physical properties of that metal. The paper contains details of the most recent attempt to obtain pure iron, and that part of it which is concerned with that object will be considered at length.

"The essential details of the bath are as follows: Two cylindrical anodes of ingot iron about 2 inches (5.08 cm.) in diameter and 5 inches (12.7 cm.) long, contained in porous clay cups; three cathodes of sheet iron, each 4 inches square; electrolyte, 25 to 30 percent $FeCl_2$ solution (made by dissolving the ingot iron in chemically pure hydrochloric acid), prepared as nearly neutral as possible; current density about 0.5 to 0.7 amp./sq. dm.; temperature during electrolysis approximately that of the room. No attempt was made to determine the yield or to secure high current efficiency. Good adherent deposits were obtained, the greatest

[77] Galvanotechnik, 1910.

[78] Bureau of Standards, Scientific Paper No. 266 (1916).

thickness being about 0.5 cm. Owing to the unfavorable current distribution when working with anodes and cathodes of such unequal size, the thickness of deposit was not uniform over all the plates. Qualitative tests of the sludge from the anode cells showed that there was an accumulation of manganese and copper derived from anode impurities. The porous cups, therefore, seemed to be of service in preventing anode impurities from migrating to the cathodes, and they were accordingly used in one of the larger baths to be described later. In another similar tank the cups were omitted. Table II shows that the cathode deposits from the bath without the cups were a little higher in copper than the others, but were otherwise of similar quality.

Much oxidation of the surface layers of the electrolyte was found as electrolysis went on, resulting in the production of basic salts of iron, which floated in the bath, and which migrated to some extent to the cathodes. With the intention of avoiding or minimizing this oxidation, the small bath was provided with a hydraulically sealed cover having windows for observation and conduits for the current leads. The air in the space above the electrolyte was displaced with purified carbon dioxide, and the electrolysis conducted as before. This method led to no marked improvement, and it was abandoned, especially as there seemed to be a tendency toward higher percentages of carbon in the cathodic deposits. Although the greater part of the sediment settled to the bottom, the bath was never quite free from turbidity caused by these basic salts, and there is no doubt that the deposits were contaminated by them in slight degree. This was of no consequence inasmuch as these impurities were either volatilized or were reduced to iron in subsequent melting operations.

The analysis of the iron stripped from cathodes of the small electrolytic bath is given in Table II. About 2 or 3 kg. was made in this bath. The large electrolytic bath is shown in Fig 1.[79] The anode cups were molded from a mixture of equal parts by volume of alundum cement and of clean white Ottawa sand; after careful drying in an oven the cups were burned at a temperature of 1000° to 1100° C., and were then found to have a satisfactory degree of porosity. The current density during elec-

[79] This figure cannot be reproduced here.

trolysis varied from 0.3 to 0.4 amp./sq. dm. The electrolyte contained 23.3 percent $FeCl_2$ (made from the ingot iron previously described) and 10.3 percent NaCl, and was nearly neutral..... The character of the deposits is shown" (in micrographs) "Deposits of 5 to 7 mm. thickness were obtained; the characteristics of these were about the same as of those made in the smaller bath. They were very hard and brittle in consequence of contamination by hydrogen. On removal from the bath and after washing with distilled water they corroded rapidly in the air."

TABLE II.

*Analyses of Electrolytic Iron from Various Sources.*

| Source | C | S | P | Mn | Si | Cu | Ni & Co. | Total | Analysis by |
|---|---|---|---|---|---|---|---|---|---|
| 1[a,b] | 0.004 | 0.002 | trace | trace | 0.003 | 0.006 | 0.011 | 0.026 | B. S. |
| 2[c,b] | 0.004 | 0.003 | trace | trace | 0.006 | 0.006 | 0.011 | 0.024 | B. S. |
| 3[d,b] | 0.004 | 0.006 | trace | trace | 0.008 | 0.006 | 0.011 | 0.035 | B. S. |
| 4[e] | 0.004 | 0.004 | trace | trace | 0.005 | 0.008 | 0.011 | 0.033 | B. S. |
| 5[f] | 0.063 | 0.002 | 0.005 | 0.009 | 0.005 | | . . . | 0.084 | Müller |
| 6[g] | 0.008 | trace | 0.002 | 0.009 | 0.014 | | . . . | 0.033 | Stead |
| 7[h] | 0.008 | 0.004 | trace | trace | 0.006 | 0.011 | . . . | 0.029 | B. S. |
| 8[i] | 0.009 | 0.003 | trace | trace | 0.006 | 0.006 | . . . | 0.024 | B. S. |

[a] B. S. (with porous cups). ["B. S." = "Bureau of Standards."]
[b] B. S. analysis of anodes from which this iron was made (percent): C = 0.013; S = 0.020; P = 0.003; Mn = 0.025; Si = 0.003; Cu = 0.024; Ni + Co = 0.021.
[c] B. S. (with porous cups).
[d] B. S. (without porous cups).
[e] B. S. (from small tank).
[f] A. Müller, Metallurgie, 1909, VI, 152.
[g] H. C. H. Carpenter.
[h] Langbein-Pfanhauser.
[i] C. F. Burgess.

*Remarks:* So far as the analyses show, it cannot be said that the purity of the iron made by Cain and his collaborators is much, if at all, superior to that produced or used by others. The same may be said of their analyses as they have said of those of others, namely, that they are incomplete. For instance, it would be surprising if no chlorine or sodium was to be found in their iron, and there is no report of hydrogen content. Unless this gas, which is admitted to be present in the iron as taken from the bath, is entirely got rid of during the subsequent refinement to

which the iron is subjected (and to get rid of it entirely is a very difficult matter),[80] it might and probably would have an important effect upon the values obtained in the determination of physical constants.[81]

### (9) *R. Kremann.*[82]

The researches of Kremann and his co-workers—J. Lorber, R. Maas, C. Th. Suchy, H. Breymesser, and others—are concerned, for the most part, with the deposition of alloys, especially nickel-iron and iron-magnesium alloys. There are, however, here and there, observations upon the deposition of iron which may be usefully noted. These will be referred to under separate headings.

(*a*) *Conditions of Deposition:* The following factors are given as favoring the deposition of iron and retarding the co-deposition of hydrogen—higher temperature and greater concentration. In neutral baths a tendency was found for oxide to be included in the deposit, but that this could be prevented by acidifying the solution, which, however, diminished the efficiency.[83]

(*b*) *The Deposit:* Regarding iron deposits, Kremann says[84]: "Iron deposited at the cathode contains hydrogen in the dissolved condition: the higher the current density and the lower the temperature, the greater the amount of the hydrogen is . . . The inclusion of hydrogen changes the mechanical properties of the iron very importantly, and it is supposed that the hydrogen content makes it hard and brittle." Kremann states it as his opinion that, primarily, the hydrogen content is not the cause of the hardness, but that this is due to the structural arrangement (*strukturelle anordnung*) of hydrogen-containing metal. The other remarks of Kremann in regard to the structure of the deposited metal are of interest: "The crystallites appear to us to be smallest in the case of material deposited from solution containing acid." The explanation given is as follows: "Separation of metal at the cathode must be looked upon as a crystallization process. In all

[80] As has lately been shown by J. Cournot, Compt. rend., 1920, **171**, 170.

[81] *cf.* Sir R. Hadfield, Jour. Iron and Steel Inst., 1913 (No. 2), p. 182.

[82] Monatsh. f. Chemie, 1913, **34**, 1757; 1914, **35**, 603, 731, and 1387; and **38**, 91 and 359.

[83] Monatsh. f. Chemie, 1917, **38**, 359 and 360.

[84] *Loc. cit.*, 360, 361.

such processes one obtains small crystals by stirring and movement, whilst large crystals are formed when the growth is undisturbed; and we hold the view that the co-separation, in the course of electrolysis, of hydrogen with the metal gives rise to stirring movement, and thus operates against the formation of large crystals."[85]

The structure of deposits formed in an iron solution containing citric acid showed nothing that resembled cementite or martensite (perlite is not mentioned). Kremann is of opinion that the organic constituent of the solution is contained in the deposit in the form of complex products, rich in carbon, which are embedded in the ferrite (much in the same way as temper carbon is) and which give rise to a brown coloration of certain areas of the deposit. In other words, one may gather from Kremann that there is nothing in the nature of an alloy formed as between the iron and carbon that is to say, nothing in the nature of steel is deposited.

*Remarks:* The author can confirm from his own experience Kremann's remarks upon the effect of the presence of free acid in the solution on the structure of iron deposits. But whether the cause of the effect produced is that given by Kremann, or is some other, seems to the author undetermined. Attention is directed to what is said concerning the deposits formed in baths containing organic substances.

### (10) *E. H. Archibald and L. A. Piguet.*[86]

It is difficult to understand the utility of the work of Archibald and Piguet; and it is still more difficult to understand in what sense they intend to be true the assertion that "The best results dealing with the electrodeposition of iron have invariably been obtained when the solutions contained organic acids." (p. 107).

In the opinion of the present author, all that is shown by the experiments of Archibald and Piguet is that a cetrain amount of

[85] *Loc. cit.*, 367 and 368. For a similar effect produced on the structure of deposits formed in the acidified chloride bath see "Experiments on the Fischer-Langbein Solution." Sieverts and Wippelmann have observed that the effect of acid upon the structure of deposited copper is to diminish the grain-size. *v.* Zeits. f. anorg. Ch., 1915, **91**, 1. *Cf.* also "The Forms of electro-deposited Iron, and the effect of acids upon its Structure," by the present author. Trans. Faraday Soc.

[86] "The Electrolytic Deposition of Iron from Organic Solvents." Trans. Roy. Soc. Canada, 1917-1918, **11**, 107.

iron can be completely extracted from a solution of acetone or acetone and water containing it, and that it can be deposited from such solutions free from carbon. They do not show that the iron is precipitated in the reguline, metallic form, or even—all of it—as iron at all; most of the deposit was, they say, in the form of a red or yellow powder, the composition of which they do not appear to have investigated. Archibald and Piguet assert, further, that "It seems that these facts could be used as a basis for the separation of iron from other metals such as aluminum and chromium;" but, as a matter of fact, their experiments do not show this at all. On the other hand, while it is true that W. R. Mott[87] came to the conclusion, as the result of many experiments, that the deposition of aluminum from acetone solution is impossible, it has for ten years or more been known that iron is precipitated from acetone solution.

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## DISCUSSION.

WM. BLUM[1]: During the war the deposition of iron was of considerable interest and was used quite extensively in England and France, particularly by the British army, for the repair of worn parts and the building up of under-dimentioned parts. In consequence there have been several researches on the electrodeposition of iron published during the last few years. Mr. Hughes, in this paper, brings the whole subject up to date in a comprehensive way. I have not heard of any cases in which iron plating has been applied in this country, and I do not know whether there is likely to be a great field for it. In looking over the work done in Europe there appear to be few cases in which they could not have done the same thing with nickel. You can get thick nickel deposits as easily as iron, and the difficulties, as shown in these papers of getting iron of good physical properties, are great.

[87] H. E. Patten and W. R. Mott, Trans. Am. Electrochem. Soc., 1909, **15**, 529. These workers used a solution of iron chloride just as did Archibald and Piguet. No mention is made by the latter of the work of the former.

[1] Chemist, Bureau of Standards, Washington, D. C.

COLIN G. FINK[2]: There are experiments outlined and some work has been done in producing electrolytic iron on a comparatively large scale, in order to take the place of Swedish iron, so as to have an independent source of pure iron. Furthermore, the increasing use of ferro-alloys as additions to steel has made it difficult to sort the scrap, and has increased the demand for Swedish iron to such an extent that the date does not seem to be distant at which the production of electrolytic iron will be a paying proposition in this country. Mr. Hughes has produced tons of pure electrolytic iron. A paper, on the use of powdered electrolytic iron, has recently been presented before the American Institute of Electrical Engineers.

W. E. RUDER[3]: Several samples of electrolytic iron which have been made under commercial conditions have come to my hand, and have been tested for magnetic properties. In every case the magnetic properties were poorer than those of the best grade of open-hearth steel. The reason for this seems evident on microscopic examination. While the metal is being deposited, it apparently carries down from solution a form of impurity, probably oxide. I have not determined just what it is, but nevertheless the material looks like a badly oxidized run of iron.

The magnetic tests bear this out; showing a lower permeability and a higher hysteresis loss, and, on account of the low conductivity, a somewhat higher eddy current loss, than pure grade of open-hearth steel normally gives. To get the best properties out of electrolytic iron it is necessary to remelt it under conditions that allow no reintroduction of impurities, and that adds considerable to the cost of the iron. Some years ago Yensen pointed out, before several societies the great advantages to be obtained magnetically, from pure iron. Mr. Yensen used in his researches, however, material which had been remelted in vacuum, which treatment removes the gases and any impurities which may be intrained or entrapped in the iron on deposit. I have examined electrolytic iron produced in Germany, and some which had been made in this country, produced under commercial conditions, and in both of these cases the material rolled from the deposited metal

[2] Consulting Electrometallurgist, New York City.
[3] Metallurgist, General Electric Co., Schenectady, N. Y.

and not remelted was poorer than we would expect from a good commercial grade of open-hearth steel made for the purpose.

BRADLEY STOUGHTON[4] (*Communicated*): In this interesting and valuable summary of a subject which bids fair to become of commercial and industrial importance, the author has omitted the work of the Sociètè "Le Fer" in France, perhaps because this has been on the industrial, rather than the laboratory, scale. It has led to what seems to be, nevertheless, the most interesting result of any researches so far carried on. Two French iron works, namely, les Fonderies at Forges de Sainte-Marie, et Gravigny, and the works of Bouchayer et Viallet, et Grenoble, have carried on the process commercially, and at least the latter is still manufacturing boiler tubes of varied sizes, and has been doing so for six years in successful competition with the established processes of boiler tube manufacture. M. Bouchayer declares that he can make thin boiler tubes, and tubes of large diameter, cheaper than he can buy them, and that they have a purity of about 99.97 percent iron. This agrees with the other analyses on page 201 of Mr. Hughes' paper.

The best published description of these works is in Le Genie Civil, August 23, 1919, and two following issues. A previous account by L. Guillet, who is one of the Directors of the Sociètè Le Fer, is in Revue de Metallurgie (Memoires), February, 1915.

The researches commenced with the work of Anthelme Boucher, whose first patent was taken out in France in 1910, and continued for some years before industrial operation was attempted. The electrolyte is ferrous chloride, the anode is cast iron scrap, and the pure iron is deposited on rotating cathodes at a density of about 1,000 amperes per square meter (107 amp./sq. ft.). Dense, smooth deposits are obtained by means of preventing as far as possible the presence of hydrogen bubbles on the cathode by the addition of depolarizers to the electrolyte.

The deposited metal is of excellent quality and ready for immediate industrial use after driving off the occluded hydrogen, by annealing in a bath of oil at a temperature near 300° C. The speed of rotation of the cathode, and the temperature of the

[4] Consulting Engineer, New York City.

electrolyte (which must be maintained absolutely constant) must be regulated in accordance with the density of the current. The concentration and depolarizing power of the electrolyte must also be maintained constant, and the circulation of the electrolyte around the anode must be as rapid as possible. Jean Escard, in Le Genie Civil, gives the following analysis of a finished tube:

| | Percent |
|---|---|
| Iron | 99.967 |
| Carbon | 0.008 |
| Manganese | 0.009 |
| Silicon | 0.014 |
| Sulphur | Traces |
| Phosphorus | 0.002 |

After annealing he describes it as being as malleable as pure copper, and this description is confirmed by tests and cold-rolling operations which have been applied to the Grenoble product in the United States.

The cost of operation per metric ton of this process is given in Bull. de la Soc. de l'Ind. Nat., 1917, No. 3, as follows:

| | |
|---|---|
| Energy (at 0.02 fr. per kw. hr.) | 86 francs |
| Cast iron (for anodes) | 100 francs |
| Other expenses | 34 francs |
| | 220 francs |

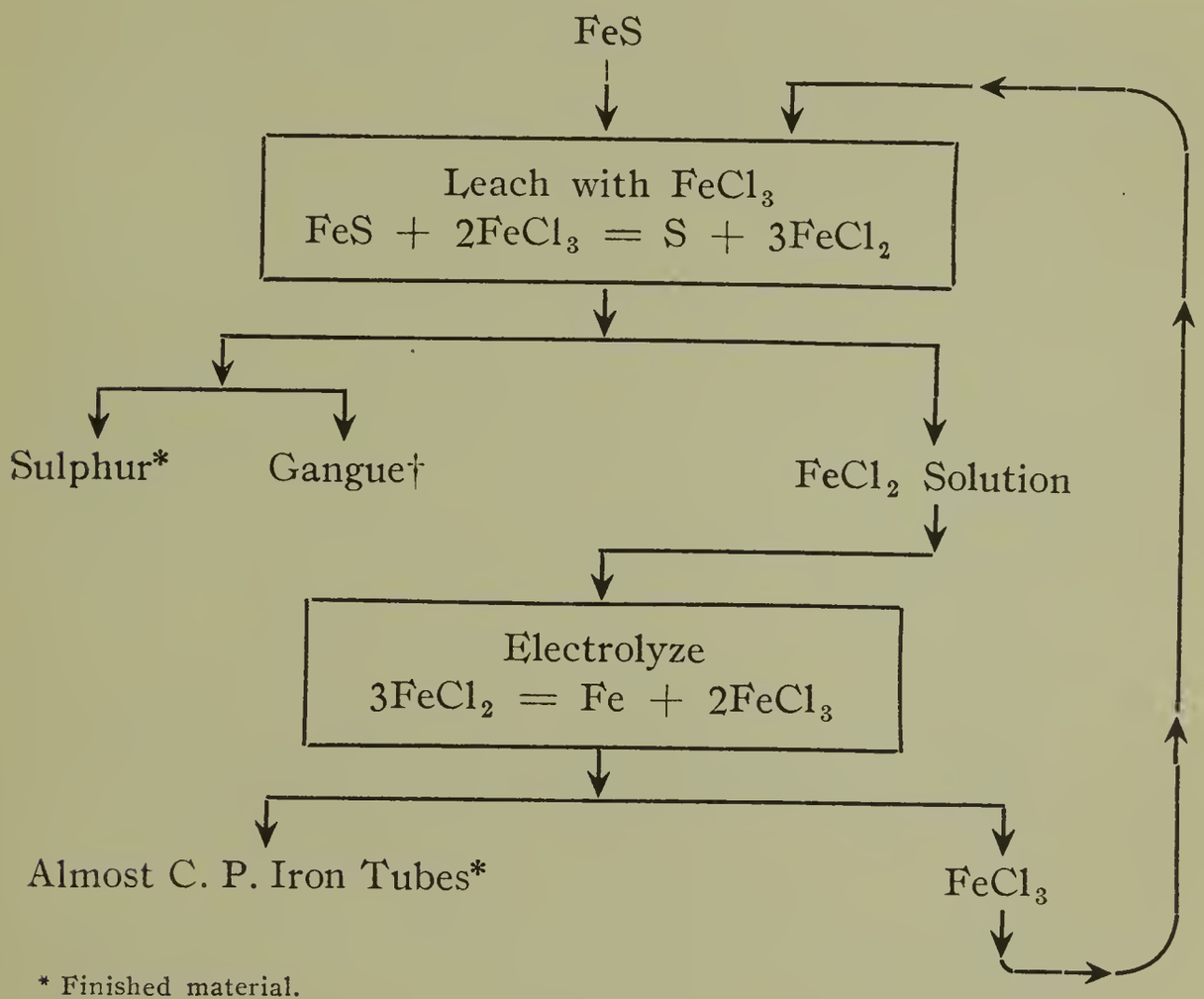
It would seem therefore that the great contribution of these French metallurgists and ironmasters to the electrodeposition of iron consisted in developing a process whereby one could secure, at competitive prices as compared to the prevailing processes of manufacture, finished articles suitable for immediate use after a simple anneal, and of a high degree of purity.

*The Eustis Process*[5]. F. A. Eustis, of Boston, and Charles P. Perin, of New York, have also developed a process, upon which researches have been carried on in the laboratories of the Massachusetts Institute of Technology, by Professor Carl Hayward, H. M. Schleicher, and Donald Belcher. This differs from the "Le Fer" process in that an insoluble anode is used and no oxidation of the electrolyte is attempted. The hot electrolyte of ferrous chloride is formed by leaching an iron ore with a solution contain-

[5] U. S. Patent, No. 1,377,822, May 10, 1921.

ing chloride, reducing the solution, and then circulating it through the electrolytic vat.

The iron is deposited on a rotating cathode, and the anode and cathode compartments are separated by a porous diaphragm of woven material, not affected by the action of the ferric chloride. A slight hydrostatic head of electrolyte prevents the ferric chloride formed at the anode from entering the cathode compartment




* Finished material.
† Waste.

through this diaphragm. Most of the researches have been carried on with a sulphide iron ore, thus securing the solution and reducing it at the same time, and the metal has been deposited in the form of tubes, which are dense, smooth, and of excellent quality.

Analyses by Andrew McCreath & Son indicate that it is more than 99.99 percent iron. The process uses no solid fuel whatever to produce finished iron articles from an ore. It would therefore enter into direct competition with electric smelting processes, but with the advantage that electrolysis will produce a ton of iron with the expenditure of much less electric energy than electric

smelting. Ferric chloride is the leaching agent and electrolysis produces ferric chloride again, so the whole process is a closed cycle, as shown by the accompanying "flow-sheet."

Pyrrhotite is the cheapest and one of the most abundant iron ores on the North American continent. On account of its sulphur content, pyrrhotite so far has been considered unsuitable for the common blast furnace process. The Eustis process is interesting from the technical standpoint, because the pyrrhotites which have been experimented upon have yielded 97 percent of their iron and sulphur in the leaching process; so that we have a simple cycle which actually turns into finished product over 95 percent of the ore that is treated. This is unique in iron metallurgy.

From the electrochemical standpoint, the Eustis process is interesting because it adds another to the increasing list of metals which are now, or soon may be, produced directly from ore to finished product by electrolysis. Mechanically considered, all equipment entering into the actual process of manufacture is of a standardized type continuously used in a number of industrial processes. It is merely a repeated application of successful operation in a new direction.

HENRY HOWARD[6]: You say the sulphur is left behind?

J. W. RICHARDS[7]: The sulphur is left behind as elemental sulphur; it is left with the gangue of the ore. He takes the sulphur as finished material, that is, available material, and the gangue as waste.

F. A. LIDBURY[8]: What anodes are used?

BRADLEY STOUGHTON (*Communicated*): They are graphite anodes.

G. W. ELMEN[9] (*Communicated*): The possibility of obtaining very pure iron by electrolytic refining is of particular interest in connection with the use of iron for magnetic purposes. It is now a well-established fact that the small percentages of impurities present in the best grades of soft iron affect the magnetic properties of the iron materially. This is especially true of carbon. A variation of a few hundredths of one percent

[6] Grasselli Chemical Co., Cleveland, O.
[7] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.
[8] Works Manager, Oldbury Electro-Chem. Co., Niagara Falls, N. Y.
[9] Western Electric Co., New York City.

of carbon in the iron used for cores in certain types of electromagnets, may result in material changes in their operating characteristics. It has, therefore, become necessary to select the iron for this purpose with extreme care. If any electrolytically refined iron which is carbon free could be obtained, at a cost of production which would permit its use commercially, this iron would probably, for magnetic purposes, be used in preference to the best grades of iron refined by other methods.

Of the two or three solutions and processes discussed in this paper which have been used to refine iron on a commercial scale, one of the best is no doubt the Fischer-Langbein process. I believe, however, that while the extreme purity and freedom from carbon of the iron produced by this process, as shown by the analysis quoted in this paper, may perhaps be obtained under laboratory conditions, it may not represent the product when produced under commercial conditions. Some years ago I had the opportunity of examining some of the iron produced commercially by this process in Germany. It was in sheets 0.014 inch (0.036 cm.) thick, and its mechanical properties resembled those of lead. Chemical analysis gave the following impurities:

| | Percent |
|---|---|
| C | 0.036 |
| Mn | None |
| P | 0.006 |
| S | 0.010 |
| Si | 0.006 |

These samples contained, therefore, as much carbon as the best grades of soft iron refined by other methods.

In addition to its extreme purity, iron refined electrolytically has, however, other properties which have made it possible to use it extensively as a substitute for hard iron wire, for cores in certain types of induction coils used in electrical transmission circuits. For this purpose the brittleness of the iron, deposited from a sulphate-chloride bath, and certain magnetic properties imparted to the iron by the process of electrolytic deposition make it of particular value. The brittle iron is ground into a fine powder and the particles insulated, and pressed into solid rings. The cores are constructed from these rings. Several hundred tons of electrolytic iron are used annually for this purpose.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, October 1, 1921, Vice-President Hinckley in the Chair.*

# ELECTROLYTIC SOLUTION AND DEPOSITION OF COPPER[1]

By T. R. Briggs[2].

Abstract.

The author modifies the theory formulated by Luther and concludes that the electrolytic behavior of copper in solutions containing copper ions may be accounted for by two electrochemical reactions (or their reverse):

$$(1)\ Cu + \oplus \rightarrow Cu^{+},\ (2)\ Cu^{+} + \oplus \rightarrow Cu^{++}.$$

The cuprous ions formed at the anode may be removed by electrolytic oxidation or by chemical means in which respective cases the copper dissolves as a bivalent and as a univalent metal. Similarly cuprous ions may be supplied at the cathode by electrolytic reduction of cupric ions or by chemical means in which respective cases copper is deposited as a bivalent and as a univalent metal. If conditions are partly electrolytic and partly chemical the copper dissolves and is deposited with an apparent valence which lies between 1 and 2. The theory advanced is applicable in general to metals other than copper. [A. D. S.]

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In discussing the electrolytic behavior of copper it is necessary to take into consideration the fact that this metal forms both cuprous and cupric ions when it is brought into contact with aqueous solutions. This fact is, of course, generally recognized at the present time and renders it necessary to place copper in the same class with metals such as chromium, iron and gold, which are known to form cations of more than one valence. It is indeed

[1] Manuscript received August 18, 1921.

[2] Department of Chemistry, Cornell University.

possible, though it has not been definitely proved, that all metals may exhibit this behavior to some extent.[3]

A general theory in regard to the electrolytic behavior of such metals has been formulated by Luther,[4] who assumed in the case of copper that three electrochemical or potential producing reactions are possible, as follows:

$$\text{I} \quad Cu + \oplus \rightarrow Cu^{+}$$
$$\text{II} \quad Cu + 2 \oplus \rightarrow Cu^{++}$$
$$\text{III} \quad Cu^{+} + \oplus \rightarrow Cu^{++}$$

The first reaction involves the change from metallic copper to cuprous ions in solution, the second reaction the change from metal to cupric ions, and the third reaction the oxidation, by electrolytic means, of cuprous to cupric ions. When copper is made anode these reactions tend to take place from left to right as written, while as a cathode immersed in a solution of a copper salt the direction of these reactions is reversed.

Luther proceeded to determine the potentials produced by the first and third reactions and showed that the third furnishes a more negative potential than the first one does. He also concluded on theoretical grounds that the potential of the second reaction must lie between the potentials of the first and third, and in the case of copper must be the mean of the two. Thus, when all the ion-concentrations are equal to unity, that is, when the solutions contain one gram-equivalent per liter of the respective ions, Luther obtained + 0.51 volt for $E_I$ and + 0.15 volt for $E_{III}$ the mean of these values, supposedly equal to $E_{II}$, being + 0.33 volt.[5] On measuring the potential of copper in cupric sulphate, which he thought must be determined by reaction II, he actually obtained + 0.33 volt, apparently a confirmation of the theory.

When copper is immersed in cupric sulphate containing no cuprous salt, the metal is known to dissolve to some extent with the formation of cuprous sulphate, quite as iron dissolves in solutions of ferric salts. The extent of corrosion is, however, far less

[3] Cf. magnesium and aluminum. Turrentine: Jour. Phys. Chem., 1908, **12**, 448.

[4] Zeit. phys. Chem., 1900, **34**, 488; 1901, **36**, 391; Cf. Foerster: Elektrochemie, 1915 (2d Ed.), 346.

[5] Cf. Foerster: Elektrochemie, 1915 (2d Ed.), 351.

than it is in the case of iron. Equilibrium is ultimately established in accordance with the following reversible reaction:

$$\text{(IV)} \qquad Cu + Cu^{++} \leftrightarrows 2Cu^{+},$$

from which one derives the equation of the equilibrium isotherm:

$$[Cu^{+}]^{2} / [Cu^{++}] = K$$

According to Luther, the reactions which lead to this "cuprous-cupric" equilibrium are electrochemical in nature and equilibrium is reached when the e f f e c t i v e potentials of the electrochemical reactions I, II, and III are equal in value. In order that they may be equal, the concentration of the cuprous ions must be small compared with that of the cupric ions, and this deduction proves to be in entire agreement with the actual facts.[6]

Furthermore, the equilibrium equation brings out the point that, at constant temperature, a fixed relation must exist between the concentration of cuprous and cupric ions in all aqueous solutions in equilibrium with copper, and that, for any given concentration of cupric ions there must be present a definite quantity of cuprous ions. Since K is known to increase as the temperature is raised, the "equilibrium" concentration of cuprous ions in any given solution must be larger the higher the temperature.

By applying the principles of the preceding paragraph and with Luther's theory as a guide, the electrolytic behavior of copper in solutions of copper salts has been explained more or less satisfactorily by assuming that the electrochemical reactions I, II, and III proceed in such wise as to maintain, during electrolysis, the nearest possible approach to chemical equilibrium between metallic copper and cuprous and cupric ion during electrolysis. The theory is not simple, however, and it is proposed in this paper to introduce certain modifications which appear greatly to clarify matters and to render possible a more systematic treatment of a complex problem.

We shall modify Luther's theory by assuming that copper can ionize in only one way, and that only as c u p r o u s ions in

[6] Molar copper sulphate in equilibrium with metallic copper at 25°C has been found to contain $3.4 \times 10^{-4}$ gram-atoms per liter of copper as cuprous sulphate. Cf. Foerster: Elektrochemie, 1915 (2d Ed.), 216.

accordance with electrochemical reaction I. In other words, we shall assume that Luther's second reaction—the direct ionization of copper to cupric ions—does not actually take place. Furthermore we shall assume that cupric ions are always produced by oxidation, either chemical or electrolytic, of cuprous ions as intermediate product. In a similar manner we shall postulate that metallic copper is deposited at the cathode by the discharge of cuprous ions and never by the discharge of cupric, and when copper is deposited from solutions of cupric salts, cupric ions must be reduced electrolytically or chemically, before actual deposition can take place. The theory may be summarized by saying that the electrolytic behavior of copper is determined by two electrochemical reactions (or their reverse) as follows:

$$\text{A} \qquad Cu + \oplus \rightarrow Cu^{+}$$
$$\text{B} \qquad Cu^{+} + \oplus \rightarrow Cu^{++}$$

The theory leads to the interesting conclusion that in the electrolytic solution or deposition of one gram-atom of copper *at least* one faraday must be transported by reaction A or its opposite, while more or less than one faraday, may be transported by B or its opposite, depending upon conditions. The *apparent valence* with which copper is dissolved or deposited can therefore never be less than one, though it may have any value greater than this.

In order to emphasize the importance of reaction A and to distinguish it from all other electrochemical reactions which may take place at the electrodes, it is proposed to term this the "fundamental" electrochemical reaction of copper. In order to make the theory general it is necessary to assume one and only one fundamental electrochemical reaction for any given metal at each electrode, and it follows necessarily that the fundamental reaction must involve the metal and its ions of lowest valence.

It should be pointed out that these assumptions do not imply that the fundamental reaction is necessarily the first to occur at an electrode, but they do require that the fundamental reaction must take place when copper is *dissolved* or *precipitated* electrolytically. The question as to which electrochemical reaction occurs first or more easily at the given electrode is

answered by considering the effective potentials of the two reactions A and B, and these potentials, in turn, are a function of the normal potentials (as determined by Luther for I and III) and the concentration of the participating ions.

The assumption of a fundamental electrochemical reaction for every metal is similar to the one made previously by Bennett and Thompson[7] to account for hydrogen and other overvoltages. They assumed that hydrogen ions are discharged invariably as monatomic hydrogen and that ordinary or molecular hydrogen is produced only by the polymerization of monatomic hydrogen as the intermediate product. In the case of copper, the present theory assumes that copper passes from metal to solution or from solution to metal during electrolysis only by passing through the intermediate stage of cuprous ions.

In terms of the present theory metallic copper is in chemical equilibrium with its ions in solution, only when the effective potential of the fundamental reaction A is equal to the potential of B. For it is generally recognized that equilibrium in the reaction,

$$Zn + 2Ag^{+} \leftrightarrows 2Ag + Zn^{++},$$

is reached, when the effective potentials of the reactions,

$$Zn + 2 \oplus \rightarrow Zn^{++} \text{ and } Ag + \oplus \rightarrow Ag^{+},$$

are equal. Since the two reactions,

$$Cu + Cu^{++} \leftrightarrows 2Cu^{+} \text{ and } Zn + 2Ag^{+} \leftrightarrows 2Ag + Zn^{++},$$

are known to be similar,[8] and since only two electrochemical reactions are necessary to account for equilibrium in the case of silver and zinc, it seems unnecessary to add a third reaction,

$$Cu + 2 \oplus \rightarrow Cu^{++},$$

as Luther does, to account for the case of copper. Also, when Luther determined, as he supposed, the potential of the reaction,

$$Cu + 2 \oplus \rightarrow Cu^{++},$$

by measuring the potential of copper against a solution of cupric sulphate, he was probably merely measuring the e q u a l poten-

[7] Trans. Am. Electrochem. Soc., 1916, 29, 271.
[8] Cf. Foerster: Elektrochemie, 1915 (2d Ed.), 348

tials of A and B, owing to the copper being practically in chemical equilibrium with an adhering film of solution "saturated" with cuprous ions.

In applying the theory to the case of copper we shall consider first the solution of copper as anode, assuming for the sake of simplicity that the metal is in chemical equilibrium with its ions in the electrolyte before electrolysis begins. It was pointed out in a previous paragraph that this condition of equilibrium requires a definite concentration of both cuprous and cupric ions in the solution phase, though the concentration of cuprous ions at room temperature is small. Suppose that current is passed and copper dissolves. In accordance with the theory just described, copper can pass into solution only through the agency of the fundamental electrochemical reaction, with the production of cuprous ions. The fundamental reaction therefore adds cuprous ions in excess to the system and tends, thereby, to destroy the state of chemical equilibrium which existed at the start. As required by the theorem of LeChatelier, the system—metal plus solution—endeavors to return to a new state of equilibrium and in doing so tends to eliminate the disturbing factor, which in this case is the excess of cuprous ions.

Cuprous ions may be eliminated in two ways in actual practice, (1) by electrolytic oxidation to cupric ions and (2) by physical or chemical reactions involving the disappearance of cuprous ions from the film of solution in contact with the anode. To what extent the two methods are employed will depend upon the chemistry and electrochemistry of the particular system in which copper is anode.

We are now in position to consider what happens in the following three cases:

Case 1. The elimination of cuprous ions is entirely electrolytic.

Case 2. The elimination of cuprous ions is entirely non-electrolytic (physical or chemical).

Case 3. The elimination of cuprous ions is partly electrolytic and partly non-electrolytic (physical or chemical).

In Case 1 all the cuprous ions formed by the fundamental reaction must ultimately be removed by electrolytic oxidation to

cupric ions, provided the concentration of cupric ions remains unchanged as the result of electrolysis. Hence for every gram-atom of copper dissolved by the fundamental reaction (involving one faraday) a gram-atom of cuprous ions must be oxidized electrolytically by reaction B (involving a second faraday). The total change may therefore be represented by the apparent reaction,

$$Cu + 2 \oplus \rightarrow Cu^{++}$$

and copper dissolves quantitatively as bivalent metal.

In Case 2, if all the cuprous ions produced by the fundamental reaction are ultimately removed by physical or chemical means, the fundamental reaction is the only electrochemical reaction involved in the process as a whole and copper dissolves electrolytically as univalent metal.

In Case 3, which is the usual case in actual practice, cuprous ions are eliminated by both electrolytic and non-electrolytic means. It follows from this that the a p p a r e n t valence with which copper dissolves electrolytically must lie between the extremes of the two preceding cases—that is, between 1 and 2. The actual value of the apparent valence will depend upon the relative effectiveness of the two methods of eliminating cuprous ions.

Case 1 (electrolytic removal of cuprous ions) is most nearly realized in practice when copper is made anode in weakly acidified copper sulphate solutions at low temperatures and in the absence of dissolved oxygen in the electrolyte. Case 2 (non-electrolytic removal of $Cu^{+}$) is most nearly realized when copper is made anode in solutions of alkali-metal cyanides or chlorides, in the absence of oxygen. Case 3 (part electrolytic and part non-electrolytic) is the case actually met with in ordinary electroplating or refinery work, and makes it clear at once why pure copper anodes dissolve in copper sulphate electrolytes with an efficiency which exceeds 100 percent.

Objection may be made to the fact that the theory requires that copper as anode should dissolve with an apparent valence never greater than 2, that is, at never l e s s than 100 percent efficiency as bivalent copper. We know that efficiencies of less than 100 per cent. are met with in practice. Whenever the apparent valence with which copper dissolves is greater than 2 and the current effi-

ciency is correspondingly less than 100 percent bivalent copper, some electrochemical reaction n o t involving the ions of copper is also taking place at the anode, and it should be borne constantly in mind that the deductions made by applying the theory to the three cases given above rest upon the tacit assumption that a l l electrochemical reactions n o t involving the ions of copper are excluded.

Cuprous ions may be eliminated c h e m i c a l l y in several ways.[9] The first is by hydrolysis in accordance with the reaction,

$$Cu^+ + HOH \leftrightarrows CuOH + H^+,$$

which results in the formation of hydrous cuprous oxide (yellow) or cuprous oxide (red). Hydrolysis may be retarded by acidifying the electrolyte, by keeping the temperature low, and by employing as electrolyte a solution in which the "equilibrium" concentration of cuprous ions is very small (copper sulphate plus alcohol, potassium cuprous cyanide, etc.). The second method of removal is by oxidation, particularly by dissolved air, supposedly in the following way:

$$2Cu^+ + O + 2H^+ \rightarrow 2Cu^{++} + HOH.$$

Oxidation is apparently greatly accelerated by warming the solution[10] The third method of removing cuprous ions is by reaction with other ions, such as chlorine or cyanogen, to form a complex ion. This method may be extremely effective, especially when copper is made anode in concentrated solutions of sodium chloride or cyanide, the reaction in the second case probably being as follows:

$$Cu^+ + 2CN^- \leftrightarrows Cu(CN)_2^-.$$

A fourth method of eliminating cuprous ions is by means of the reaction,

$$2Cu^+ \rightarrow Cu + Cu^{++},$$

with the production of finely divided copper, which may form a slime on the bottom of the vessel containing the electrolyte (copper in refinery slimes) or may even adhere more or less firmly

[9] Cf. Foerster: Elektrochemie, 1915, 437.
[10] Cf. Foerster: Elektrochemie, 1915, 437.

to the anode.[11] This reaction can take place only when the cuprous ion concentration exceeds the value necessary for equilibrium with copper.

When copper is made anode in cupric sulphate, cuprous ions are formed by the fundamental electrochemical reaction and the metal dissolves. After the cuprous ion concentration reaches a certain value in the film of solution in contact with the anode, electrolytic oxidation begins to occur and cupric ions are formed. But while cuprous ions are being thrown off from the anode, hydrolysis and chemical oxidation of these ions may take place, particularly if the electrolyte is warmed and only very slightly acid. It may easily happen, therefore, that, if cuprous ions are generated only very slowly, or, in other words, if the anode current density is small, the cuprous ion-concentration may not increase sufficiently to permit electrolytic oxidation to take place. The elimination of cuprous ions will be entirely chemical. Under such circumstances copper will dissolve with a valence of 1, cuprous oxide being formed to some extent.

As the current density at the anode is increased, the rate at which cuprous ions are produced becomes proportionately greater and their concentration tends to rise; the latter condition makes it possible for electrolytic oxidation to eliminate an increasing proportion of the cuprous ions as the current density is made greater. In this way, it is possible to account for the fact that the apparent valence with which copper dissolves in copper sulphate increases as the anode current density is made moderately great.[12] This statement might be expressed in another way by saying that with increasing current density, the anode current efficiency of copper sulphate decreases and becomes more nearly equal to 100 percent (copper bivalent).

The theory makes it possible to state the conditions under which copper anodes will dissolve in solutions of cupric sulphate with the nearest approach to 100 percent efficiency (valence 2). They are in brief:

1. Exclusion of all extraneous electrochemical reactions not involving cuprous and cupric ions.

[11] Cf. Foerster: Electrochemie, 1915, 441.
[12] Cf. Foerster: Elektrochemie. 1915, 441.

2. Exclusion of all chemical (non-electrolytic) processes leading to the elimination of cuprous ions.

3. Electrolytic oxidation of all cuprous ions produced by the fundamental reaction at the anode.

On making copper anode in moderately concentrated solutions of sodium chloride or cyanide, it dissolves as univalent metal, provided passivity does not interfere. Sodium cuprous chloride or sodium cuprous cyanide is formed. The concentration of cuprous ions in either of these solutions is almost zero, provided an excess of $Cl^-$ or $CN^-$ ions is present. Accordingly, as fast as the fundamental electrochemical reaction produces free cuprous ions at the anode, these ions are removed chemically to form a stable complex anion, as explained in a previous paragraph.

When copper is deposited at the cathode, this deposition can be brought about only by the discharge of cuprous ions in accordance with the present theory. If the solution is in chemical equilibrium with metallic copper when electrolysis begins, the discharge of cuprous ions by the fundamental reaction tends to upset this original condition of equilibrium, and to restore the latter, more cuprous ions must be produced in some manner. It is possible to produce the cuprous ions needed by the fundamental reaction in two ways: (1) by electrolytic reduction of cupric ions, (2) by chemical (or physical) formation of cuprous ions from any available source.

If no other electrochemical reactions take place at the cathode, and if all the cuprous ions which the fundamental reaction discharges as metallic copper are supplied by electrolytic reduction of cupric ions, it is obvious that copper will be deposited quantitatively as bivalent metal. Secondly, if the cuprous ions are supplied entirely by chemical (non-electrolytic) means, copper will be deposited as univalent metal. It follows, therefore, that if the necessary cuprous ions are supplied both by electrolytic reduction and by chemical means, the apparent valence with which copper is deposited will be between 1 and 2.

Suppose, however, that the fundamental electrochemical reaction is not the only factor involved in the disappearance of cuprous ions. The theory demands only that the fundamental reaction be the sole reaction involved in the deposition of copper. As

a matter of fact, when copper is deposited electrolytically from cupric sulphate solutions, cuprous ions are removed from solution not only by deposition, but also by hydrolysis and chemical oxidation, under ordinary circumstances. Now if the necessary cuprous ions are supplied entirely by electrolytic reduction, and this is the case in cupric sulphate, the electrochemical reaction,

$$Cu^{++} + \ominus \rightarrow Cu^{+},$$

will be called upon to furnish more cuprous ions than the fundamental reaction will discharge as copper. Therefore more than two faradays will be required to deposit a gram-atom of metal and the apparent valence with which copper is deposited will be greater than 2. In other words, copper will be deposited at less than 100 percent current efficiency which is exactly the case in practice.

At low cathode current densities, cuprous ions cannot be discharged by the fundamental reaction and copper cannot be deposited until the cuprous ion concentration at the cathode becomes greater than the value necessary for the cuprous-cupric equilibrium. Cuprous ions may nevertheless be removed by hydrolysis or by chemical oxidation when the concentration of cuprous ions is less than the equilibrium value referred to above. It may thus happen that hydrolysis (and oxidation) may remove cuprous ions as fast as they can be produced by electrolytic reduction of cupric ions and current will pass without depositing copper, cuprous oxide being precipitated instead. It follows that the higher is the concentration of cuprous ions necessary for the cuprous-cupric equilibrium, and the lower the current density, the greater is the probability that no copper will be deposited at the cathode as current passes. Since the necessary equilibrium concentration of cuprous ions in copper sulphate is known to be greater at higher temperatures than at low, and since hydrolysis of cuprous sulphate is greatest in hot, neutral solutions of this salt, it is possible to account for the fact that from hot, neutral copper sulphate at low current densities, no copper is deposited, but cuprous oxide is precipitated instead.

As the cathode current density is increased, discharge of cuprous ions becomes possible and takes place; furthermore, the

number of cuprous ions removed chemically decreases relatively to the number discharged electrolytically as copper. Hence the cathode current efficiency tends to rise, and will rise, provided no other electrochemical reactions, such as discharge of hydrogen ions, make their appearance as the current density grows larger.

On the basis of the present theory we are in position to deduce the conditions under which copper is deposited at the cathode, with the nearest approach to 100 percent current efficiency, from solutions of copper sulphate. The current density should not be too small. The temperature should be low. The electrolyte should be slightly acidified to arrest hydrolysis, but should not contain too much acid for fear of liberating hydrogen at the cathode. In short it is essential to prevent, so far as possible, all forms of chemical removal of cuprous ions from solution. It will be observed that these are precisely the conditions, which, at the anode, lead to 100 percent current efficiency in the corrosion of copper.

In the copper-copper sulphate coulometer,[13] alcohol is added to increase the cathode current efficiency, for in the coulometer it is obvious that the nearest possible approach to 100 percent deposition is essential. Alcohol probably retards oxidation of cuprous ions by air (being probably oxidized instead) and it is known to force back the ionization of cupric-sulphate, thus decreasing the concentration of cuprous ions required by the cuprous-cupric equilibrium. Oxidation and hydrolysis of cuprous ions are therefore made less, though the electrochemical reactions are not affected if the voltage at the cathode be raised. It follows from the previous discussion that addition of alcohol in the coulometer causes copper to be deposited more nearly quantitatively as bivalent metal.

In the deposition of copper from solutions of sodium cuprous chloride or cyanide, cuprous ions cannot be formed by electrolytic reduction of cupric ions save in inappreciable quantities. In these solutions the cuprous ions required by the fundamental electrochemical reaction are supplied by dissociation of the complex cuprous chloride or cuprous cyanide anions, that is, by chemical (non-electrolytic) means. Furthermore, since the equilibrium and

[13] Cf. Foerster: Elektrochemie, 1915 (2d Ed.), 45.

actual concentration of cuprous ions is extremely small in these electrolytes, hydrolysis and oxidation by air are inappreciable. It follows therefore that copper tends to be deposited as univalent metal, and will do so if no outside electrochemical reactions take place at the cathode.

The results of this paper may be summarized as follows:

(1) The electrolytic behavior of copper in solutions containing copper ions may be accounted for by means of two electrochemical processes, and it is unnecessary to assume three reactions as Luther does.

(2) These two electrochemical processes are first, the change from copper to cuprous ion or the reverse, and second, the change from cuprous to cupric ion or the reverse.

(3) When copper dissolves electrolytically at the anode it can do so only through the agency of the first electrolytic process, with the formation of cuprous ions. When copper is deposited at the cathode, similarly, it can be so deposited only by the discharge of cuprous ions. The loss of copper at the anode and the gain at the cathode are a direct measure of the extent to which these electrochemical processes have taken place.

(4) It is proposed, therefore, to distinguish these electrochemical processes:

$$Cu + \oplus \rightarrow Cu^{+} \text{ and } Cu^{+} + \ominus \rightarrow Cu$$

by the term "fundamental" electrochemical reactions.

(5) The cuprous ions formed by the fundamental electrochemical reaction at the anode may be removed either by electrolytic oxidation or by chemical means, depending upon conditions.

(6) If the removal of cuprous ions is entirely electrolytic, copper dissolves as bivalent metal. If removal is entirely chemical, copper dissolves as univalent metal. If removal is partly electrolytic and partly chemical copper dissolves with an apparent valence which is greater than 1 but less than 2.

(7) At the cathode, cuprous ions necessary for the fundamental electrochemical reaction may be supplied either by electrolytic reduction of cupric ions or by chemical means from any available source.

(8) If cuprous ions are supplied entirely by electrolytic reduction, copper is deposited as bivalent metal. If cuprous ions are supplied entirely by chemical means copper is deposited as univalent metal. If both methods are employed, the apparent valence lies between 1 and 2.

(9) If, however, cuprous ions are supplied entirely by electrolytic reduction and cuprous ions are removed from solution, not only by the fundamental reaction, but also by chemical means such as hydrolysis, copper is deposited with an apparent valence greater than 2.

(10) The theory has been applied to the electrolytic behavior of copper in cyanide, chloride and sulphate electrolytes.

(11) The use of alcohol in the copper coulometer has been considered from the point of view of the theory.

(12) The theory outlined in this paper is a general one and can be applied to metals other than copper.

*Cornell University.*

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## DISCUSSION.

WM. BLUM[1]: The theory proposed appears to simplify the consideration of the factors which govern the anode and cathode efficiencies in copper solutions. This is especially important in the operation of acid copper solutions, where the excess anode efficiency results in the consumption of acid and the accumulation of copper sulphate.

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# ELECTROMETALLURGY OF ZINC.[1]

By W. R. Ingalls.[2]


## Abstract.

The author discusses the developments in electrolytic zinc extraction process. This method conducted on a large commercial scale and under favorable conditions permits of zinc production on sufficiently low terms to meet any competition. The progress in electrothemic smelting in Scandinavia is set forth. Power consumption in the electrolytic process, according to the author, will be less per ton of ore than in the electrothermic, with a resulting high grade spelter. [A. D. S.]


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Zinc is now being extracted commercially from its ores with the aid of electricity in two ways, viz., electrolytically and electrothermically. Both methods are of interest to the electrical engineer in that they employ electrical energy in great volume, but there the similarity ends. The electrolytic process belongs to the field of electrometallurgy. The electrothermic process does not, except by the broadest construction of terms. The electrothermic process is one of reduction and distillation and the principles that govern it are the same as those governing reduction and distillation by the common pyrometallurgical process. The main difference is in the manner of heating. In the pyrometallurgical process the reduction and distillation are effected in retorts heated externally. In the electrothermic process the work is done in a furnace, *i.e.*, a retort, heated internally. This method of heating permits the use of a very much larger retort than pyrometallurgically, and also permits complete scorification of the gangue

[1] Manuscript received August 11, 1921.

[2] Consulting Mining and Metallurgical Engineer, New York.

of the ore, its fusion, and its removal from the furnace or retort by tapping.

When the electrolytic process was first introduced, in 1916, I prophesied its success and the enormous influence that it would have on zinc production, but I foresaw its limitations to especially favorable conditions. In other words, it seemed to me that the experience in the zinc industry would be similar to what it had been in the sulphuric acid industry, following the introduction of the catalytic process. At that time it was prophesied that the chamber process would be supplanted, but in fact that did not happen at all. I never had any idea that electrolytic zinc extraction would displace distillation, but I appreciated that the electrolytic process had come to stay, and could meet any competition when introduced under suitably favorable conditions. My forecast has been exactly verified by experience. Some of the small electrolytic plants that were erected and operated during the war have been dismantled since then, but the great plants at Great Falls, Trail, and Risdon have continued in operation, and indeed upon a larger and larger scale. The Risdon plant is now being enlarged to a capacity for the production of about 40,000 tons of spelter per annum. The completion of the work that will give such a capacity is to be expected about the end of 1921 or early in 1922. With such a capacity for Risdon, with Great Falls at 60,000 tons per annum and Trail at 10,000 tons, and with one or two smaller plants, the world will have a capacity for the production of electrolytic zinc at the rate of about 120,000 tons per annum, which will be upward of 10 percent of the rate of the world's total pre-war production of spelter. This can not fail to be an important factor in the zinc industry. Of course, even the present production, combined with the production of high-grade spelter by distillation, has so increased the supply of that class of zinc that the old premium for it has practically disappeared.

In the course of its development great improvements have been made in the electrolytic process. For example, it has become possible so to roast the ore that no sulphuric acid is required for the lixiviation of the zinc; the removal of impurities interfering with the electrolysis has become much more easily manageable; and so on, In the light of these developments the limitations of

the electrolytic process do not seem to me to be so severe as they did four years ago. In other words, I can now see the electrolytic process as a more powerful competitor of distillation. However, the factors remain that the electrolytic process must be conducted on a large scale and the cost of plant per unit of capacity is greater than that of the ordinary plant.

Frederick Laist, of the Anaconda Company, in a recent contribution respecting the electrolytic process said the following:

"With the development of the process and the extension of our operations, my optimism as to the future of electrolytic zinc has steadily grown, until now I am not sure but that we will yet see electrolytic plants operating on high-grade concentrates and actually producing their power by the combustion of coal or oil or gas. This statement may seem somewhat extreme, but it is based on the following general premises:

"1st. The fuel required for distillation and reduction of a ton of zinc in a modern retort plant will, when burned in an efficient modern power plant, generate sufficient electric energy to deposit a ton of zinc from sulphate solution.

"2nd. The labor required for producing a ton of zinc electrolytically from a given concentrate will be no more than one-third the labor required by the furnace method."

I am not prepared yet to go quite so far as Mr. Laist. Indeed, the conditions of electrolytic zinc extraction are so variable, according to the grade and quality of the ore, that any broad generalization might be dangerous, unless it were accompanied by many qualifications and reservations. However, I am willing to say under the most favorable conditions, as for example at Great Falls and Risdon, electrolytic zinc can be produced on terms so low as to permit it to meet any competition. I conceive the possibility, moreover, that in some places electrolytic extraction might be profitably substituted for the pyrometallurgical process as now practiced. On the other hand, I believe that the ordinary method of zinc distillation is capable of important improvements, and if the existing zinc distillers be pressed by threatened competition they will make such improvements.

The electrolytic process, as practiced everywhere, comprises two steps, *viz.*, the hydrometallurgical and the electrometallurgical. In the hydrometallurgical division the operations are to

bring the zinc into solution and to purify the solution. This part of the process is carried out just as it might be for the preparation of pure zinc sulphate solution for the manufacture of lithopone or any other purpose. In the preparation of the solution for electrolysis, however, great care is necessary in the removal of some elements, the presence of which must be reduced to perhaps a milligram per liter. In practice I suppose that the most serious difficulty has been experienced with cobalt and chlorine. However, as I have previously remarked, the trouble resulting from impurities has become less and less vexatious as experience with the process has been acquired. Given the proper kind of electrolyte there is no difficulty in depositing the zinc. The practice everywhere is to use stationary cathodes of sheet aluminum, from which the deposits of zinc are stripped after 48 hours. The deposition is effected by the use of a current density of about 25 amperes per square foot. Revolving circular cathodes have been tried but have been abandoned. Deposition by the use of greatly increased current density is in contemplation. Theoretically this presents prospects for improvement in practice in several ways, but there are some disadvantages.

The technology of electrolytic zinc extraction has been fully and ably described in two recent papers; one by Herbert R. Hanley, in Mining and Scientific Press, Dec. 4, 1920; the other by Frederick Laist, F. F. Frick, J. O. Elton, and R. B. Caples, presented at the New York meeting of the American Institute of Mining and Metallurgical Engineers, February, 1921.

Electrothermic smelting has been practiced on a commercial scale in Scandinavia, especially at Trollhattan in Sweden and Sarpsborg in Norway. Besides these, there are one or two small plants. A new plant is being built at Glomfjord. This is to have capacity for smelting 60,000 metric tons of ore per annum. At the end of 1920 it had not been completed, but construction was well advanced. The electric furnaces used for ore smelting in Scandinavia are resistance furnaces, and are designed and run as combined zinc and lead smelting furnaces, both zinc and lead being obtained in the same operation, the gangue of the ore being fluxed and drawn off as slag. In the smelting at Trollhattan until within a year or two the idea was to condense spelter directly from the distillation furnace. In so doing there was

experienced the common difficulty in the matter of condensation, an unduly large proportion of the zinc being condensed as blue powder. We know now that that is inherent to any zinc ore reduction and distillation process that is carried on continuously. The common process is conducted intermittently and in stages. In the first stage there is an expulsion of oxidizing gases. After they have been driven off, and when the effluent gas becomes essentially carbon monoxide the temperature of the furnace is raised to the point of zinc reduction and distillation, and in such an atmosphere condensation of the zinc mainly as spelter can be effected. In a furnace operated continuously there can be no such control of gaseous conditions, and as fresh ore is charged into the furnace there is a constant development of oxidizing gases, and coincidentally there is more or less dusting. The entrainment of mechanical dust with the stream of gas and vapor constitutes an additional condition adverse to condensation as spelter. The continuous reduction, distillation, and condensation of zinc (as spelter), requires therefore the conditions of a two-stage operation, just as there is in the common pyrometallurgy. With a continuously operating furnace there must be either a preliminary stage of pre-reduction in another furnace, or there must be a subsequent stage of blue powder treatment, also in another furnace. Whichever be the choice, there are two stages or two steps.

The Trollhattan metallurgists adopted the method of (1) reduction and distillation and (2) blue powder retreatment. The latter was done by redistillation in an electric furnace, but this was found to be unduly expensive. The discovery was then made that the blue powder could be melted down in a comparatively inexpensive way if subjected to heating to the melting point of zinc and at the same time to a rubbing action.

In the new process recently developed at Trollhattan, which is also to be applied at Glomfjord, the resistance furnaces are run at high temperatures, the lead being completely volatilized and no attempt being made to condense the zinc as spelter. The furnace is operated on the principle of producing a highly silicious slag, which commonly contains about 50 percent of silica, and creates conditions favorable to a high degree of zinc expulsion, *i.e.*, the percentage of zinc scorified and retained by the slag is

relatively small. The vapor is rapidly cooled, the metals condensing as powder, which is subsequently melted down, affording a very leady spelter, which is finally refined by redistillation in an electric arc furnace, but of course, an ordinary grade of spelter can be produced by simple gravity refining. The ore smelting furnaces have now been built and successfully operated for large capacity, as much as 12,000 kg. of ore per 24 hours being smelted in a single furnace. This in itself is an achievement beyond what anyone else has accomplished in this field and is to the credit of the Swedish metallurgists.

I have confined myself in this paper to electrolytic zinc extraction and electrothermic smelting as the two processes are commercially practiced. I have scarcely more than hinted at experimental work that is going on in both fields and may or may not result in improvements. As between the electrolytic and electrothermic methods I am constrained to limit myself to the broadest indications. In the electrolytic process the power requirement bears substantially a direct relation to the zinc content of the ore under treatment, for the power in the main is used directly for the electrolysis of zinc sulphate and is proportional to the amount of zinc that is deposited. In electrothermic smelting the condition is different, inasmuch as energy is consumed not only for the reduction of zinc oxide, but also for the reduction of other metallic oxides and the scorification of the gangue. As the percentage of zinc in the ore increases, the amount of other work must be done in the furnace decreases, with the result that the readings of the wattmeters will not be proportional to the zinc production. In general I think I may say that the consumption of electrical energy in the electrolytic process will be less per ton of ore than in the electrothermic. However, the whole subject, together with economic comparison with the pyrometallurgical process, is too complicated to take up in a brief paper.

There is, however, one point upon which I may well touch, viz., the grade of the spelter produced. The electrolytic process results in a spelter of high grade of purity. High-grade spelter may be made by the electrothermic process if refining be done by redistillation, but so also may it be made by redistilling spelter produced in any way if the crude spelter be not cadmium-bearing. High-grade spelter has some properties that ordinary spel-

ter does not possess. It is relatively soft and it may be worked mechanically in ways that spelter that is only a little harder can not be. Heretofore, when high-grade spelter was produced only in limited quantity a substantial premium for it could be realized, but the production of this quality of metal has already exceeded the demand for it that is willing to pay a premium, and consequently the premium has disappeared. There are some important uses for which a spelter that has a certain hardness, or other qualities arising from impurities, is desirable. Therefore we are likely to see high-grade spelter being deliberately contaminated by the addition of a certain percentage of cadmium or lead in order to meet the requirements of certain customers. The producer of high-grade spelter will have only the advantage that he can guarantee absolutely the composition of the metal that he is furnishing. It is certain that the ability to produce high-grade spelter can not henceforth be viewed as an advantage pertaining to either the electrolytic or electrothermic processes that is capable of being translated into a premium of cents per pound in the market place.

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## DISCUSSION.

EDWIN W. HALE[1] (*Communicated*): Mr. Ingalls' paper is a good boost for the electrolytic process, but naturally he cannot do the same for the electrothermic process as Woolsey McA. Johnson's successful preliminary work has never had the practical test it deserved.[2] With good prereduction of the charge before it entered the electric furnace, there was no blue powder problem. The percentage of zinc vapor entering the condenser and there collected as liquid metal, was about 90 percent. The fact that the electrothermic process is a two-stage one puts it at no disadvantage as compared to the electrolytic which is also a two-stage process. Mr. Ingalls' impression or 'surmise' that electrolytic smelting would take less power per ton of metal than the electrothermic, may or may not be so. My electric smelting work seemed to show a safe estimate for power con-

[1] New York City.

[2] U. S. Patents Nos. 1,150.271, 1,165,371, 1,244,504 et al.

sumption to be 1600 kw. hours on a 35 percent Zn ore. But in addition to the zinc we recovered the lead as base bullion and copper as matte.[3] With an 8 to 10 percent lead content the power consumption would seem to have every chance of comparing favorably with the electrolytic, on the basis of metal produced.

The big advantage of electro-thermic smelting, to which Mr. Ingalls does not refer, is the automatic saving of the byproducts. In the electrolytic process the residue from the leaching must be smelted for its lead and silver; and the amount of this residue, other things being equal, represents the monetary advantage per ton of ore of the electrothermic process. The recovery of the lead and silver is made at the same time the zinc is recovered. If in the electrolytic process, there is a 50 percent residue from the leaching tanks and it costs $4.00 a ton to smelt it, this represents $2.00 a ton advantage to the electrothermic.

It is a great pity that Mr. Johnson's work has never received the practical demonstration it so plainly deserved. Zinc smelting as carried out today is proverbially the most wasteful and inefficient of our metallurgical processes. I am fully convinced that electrothermic smelting of zinc is commercially feasible and practical, more efficient and cheaper, than either the present retort process or the recently developed electrolytic process.

J. W. Richards[4]: I inspected the Swedish zinc plants this summer, and I do not think that the term resistance furnace properly applies to their zinc ore furnaces. The furnaces are run with three-phase electrodes, and are of the buried arc type. It is interesting to know that the Swedish Company had fourteen of these large furnaces, and that at first they did not operate properly. They then started to re-design them, and at the present time three of these furnaces, re-designed, are working quite satisfactorily, so that it is the intention of the company to re-design the other eleven as well.

I gave them this piece of advice, that I thought they should go slow about re-designing the other eleven until they found whether or not they could apply the continuous Söderberg electrodes to their furnaces. They were using the ordinary electrodes,

[3] Min. Scient. Press, 1913, **107**, 974.

[4] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

screwed one on to the other, and had a graveyard as large as this room filled up three feet high with pieces of electrodes anywhere from fragments up to half lengths. There was a large amount of profit and possibly dividends represented in this graveyard of electrodes, and I told them that I thought that the continuous electrode could be applied to their furnace. I think it would be no more difficult than applying it to the Heroult steel furnace, as is now being done.

The furnace which works up the blue powder by rubbing it together and recovering the zinc as coherent metal is the invention of Mr. C. E. Cornelius.[5] His name is not given by Mr. Ingalls, but the furnace will be known as the Cornelius furnace. Mr. Cornelius has sold the rights for the use of it for blue powder to this Swedish zinc company. I saw his furnace in operation; it is a remarkable thing that can take blue powder and extract sixty-five or seventy percent of its metallic contents as good liquid metal. The residue goes back into the ore furnaces for re-treatment. It is an entire novelty in the zinc industry to take the blue powder and extract so much of the metal in an electrically heated furnace. I do not know whether patents have been granted Mr. Cornelius. If not, they will soon be granted.[6] It is Mr. Cornelius also who is putting up the plant at Glumfiork.

Three or four of the zinc works in Scandinavia have also been working on an interesting alloy, which is perhaps worth mentioning here, and that is an alloy the Germans used during the war, an alloy of ninety percent zinc, four percent copper, four percent aluminum and two percent iron and antimony. I think it was used for time fuses on shells. After the war there were thousands of tons of that alloy available, and almost all of it was bought up by the Scandinavians. They distill the zinc out of it and two or three different types of electric distillation furnaces are in use. The residue, an alloy of copper and aluminum is sold to copper works, where the aluminum is slagged off and the copper recovered. There have been thirty or forty thousand tons altogether of this zinc-copper-aluminum alloy brought to Scandinavia and treated there in electric distillation furnaces.

[5] Chem. & Met. Eng., 1922, 26, 35.

[6] Brit. Pat. 168,018, Oct. 12, 1921—Ed.

C. S. WITHERELL[7]: Referring to the Swedish electrothermic process, may I ask what are the lead contents?

J. W. RICHARDS: The lead contents of the ore are rather high and the furnaces are run at such elevated temperatures that the lead is practically all volatilized together with the zinc.

C. S. WITHERELL: But I mean the resulting zinc. How high is that in lead?

J. W. RICHARDS: The blue powder treated in the Cornelius furnace produces a very leady zinc. I have no analysis, but I should think it is probably fifteen or twenty percent lead. But, according to Mr. Cornelius, this product is re-distilled. The zinc is distilled away, leaving the lead behind. This is done in furnaces of the DeLaval arc type.

C. S. WITHERELL: Relative to the disappearing premium on electrolytic zinc, this premium was paid in the past for particularly pure grades of zinc, electrolytic or of other source, by the alloy makers, in order to obtain a metal sufficiently free from deleterious impurities such as lead, antimony, arsenic, iron, etc., for making certain high-grade alloys, mostly copper-zinc alloys.

Before the advent of commercial electrolytic zinc, there was only one source of importance of pure zinc, namely that put on the market as "Horsehead" brand by the New Jersey Zinc Co. Naturally this brand was in great demand by the makers of high-grade alloys, and since there was a limited supply it could command a premium. One of the most undesirable impurities found in commercial zinc that seems to be a subject of strict specification is lead. Zinc from most other sources than electrolytic contains at least one or two hundredths of one percent lead. Many of the commoner brands, namely the brands derived from the distillation of roasted sulphides, most of which contain a small amount of lead, may run up to a few tenths of a percent in lead.

Since even one or two hundredths of a percent lead gives trouble in certain copper-zinc alloys, the alloy makers in consequence

[7] Metallurgical Engineer, New York City.

look to the copper refineries to supply copper ingots practically free from lead. In fact they specify that electrolytic copper ingots shall not contain more than 0.005 percent lead. In other words, they look to the copper refinery to make good in the purity of their product to offset the lack of purity, particularly in regard to lead, of even the purest brands of zinc that existed before the advent of electrolytic zinc.

The present electrolytic zinc production capacity is more than enough to supply the pure zinc needed for specially high-grade alloys used under peace conditions, hence as would be expected the premium has practically fallen away. But the extremely high purity of the electrolytic zinc, combined with its assured plentiful supply, has had the effect of educating the makers of all kinds of zinc alloys that pure zinc is preferable. Hence they have made specifications calling for a more pure zinc in standard grades.

Since the electrolytic zinc and possibly the "Horsehead" brand are the only kinds that can meet specifications without additional treatment for purifying, the other kinds, for example that produced by distillation from roasted sulphide ores, will have to be sold at a lower price as an inferior grade. Therefore, while the special premium for pure zinc is disappearing, in effect there still is a premium due to raising the standard of purity for commercial zinc to such an extent that competitors to electrolytic zinc will either be forced to sell at a lower price, or stand the expense of additional treatment.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, October 1, 1921, President Acheson Smith in the Chair.*

# STUDIES ON THE ZINC CYANIDE PLATING SOLUTION.[1]

By Chris. J. Wernlund.[2]

## INTRODUCTORY REMARKS.

The very numerous and trying difficulties encountered in the zinc cyanide plating industry made a further scientific study of this type of solution a necessity. The general aim of this work has been the evolution of a zinc cyanide plating solution which would operate successfully under the most trying commercial conditions, *i.e.*, at very high current densities in mechanical zinc plating units where the cleaning of the work is often poor. Since this field is practically a new one as far as scientific published data are concerned, a great deal of work has been found necessary for the successful solution of this problem. Though the work is far from complete it is felt that enough scientific data have been gathered to be of interest to this society and to render a much needed service to the zinc plating industry.

## RESUME OF THE ZINC CYANIDE PLATING LITERATURE.

The fact that zinc can be deposited from an alkali cyanide solution was first utilized only for the electrolytic determination of the metal. Among the earliest to publish methods of zinc analysis by the addition of excess potassium cyanide to the zinc salt solution we may mention the work of Beilstein and Jawein,[3] Luckow,[4] Moore[5] and Vortmann.[6] Later workers found difficulty in removing all of the zinc from the solution until F. Spitzer[7] showed that the solution gave up the last of its zinc only when the last of the cyanide was oxidized to cyanate.

[1] Manuscript received September 8, 1921. Preliminary paper No. 1.
[2] Electrochemical Research Laboratory of the Roessler & Hasslacher Chemical Co., Perth Amboy, N. J.
[3] Ber. d. Deutsch. chem. Gesl., 1879, **12**, 446.
[4] Zeit. f. analyt. chemie, 1880, **19**, 1 f.
[5] Chem. News, 1886, **53**, 209.
[6] Monat., **14**, 537.
[7] Electrochemisches Zeit., 1905, 391.

Among the earliest published work on the zinc cyanide plating solution for obtaining a zinc deposit is that of R. C. Snowden.[8] This author used a solution made up as follows: 1 g. $ZnSO_4.7H_2O$ was dissolved in 20-30 cc. of water; potassium cyanide solution was added until the precipitated zinc cyanide was redissolved. This solution was then diluted to 150 cc. per gram of hydrated zinc sulphate. The author states that this solution can be successfully used at any temperature with a current density of 5.0 amp./sq. dm. It is interesting to note that the zinc cyanide content of this solution is only 0.767 ounce per gallon (5.7 g/L.).

One of the first to recommend the use of the zinc cyanide plating solution for the commercial rust proofing of steel, is C. H. Proctor.[9] The formula he first recommended is as follows:

| | |
|---|---|
| $Zn(CN)_2$ | 3 oz. |
| NaCN | 2.5 " |
| NaOH | 2.5 " |
| $Al_2(SO_4)_3$ | 0.25 " |
| Water | 1 gal. |
| Temp. | 43 to 44°C. (110 to 111° F.) |

Later this writer has recommended the following formulas[10]:

No. 1—Morgan Arsenal Solution.

| | |
|---|---|
| Water | 1 gal. |
| $Zn(CN)_2$ | 8 oz. |
| NaCN | 7 " |
| NaOH (76 percent) | 3 oz./gal. |
| $Na_2CO_3$ | 1.5 oz. |
| $Al_2(SO_4)_3$ | 0.5 " |
| Licorice | $\frac{1}{16}$ " |

No. 2—Stainless Zinc Solution.

| | |
|---|---|
| Water | 1 gal. |
| $Zn(CN)_2$ | 8 oz. |
| NaCN | 7 " |
| $Na_2SO_4$ | 4 " |
| NaF | 1 " |
| NaOH (76 percent) | 0.5 " |
| Corn Syrup | 0.5 " |

F. J. Liscomb[11] has published two zinc cyanide formulas in which the following compositions are given:

| | Formula No. 1 | | Formula No. 2 | |
|---|---|---|---|---|
| | Oz./gal. | g./lit. | Oz./gal. | g./lit. |
| $Zn(CN)_2$ | 10 | 75 | 10 | 75 |
| NaCN | 4 | 30 | 8 | 60 |
| NaOH | 8 | 60 | 4 | 30 |

[8] T. A. E. S., 1907, **11**, 131-33.
[9] Metal Ind., 1917, **15**, 152.
[10] Metal Ind., 1920, **18**, 478, and Metal Ind., 1921, **19**, 199.
[11] Brass World, January, 1919, 67.

T. C. Eichstaedt[12] describes the process of electro-galvanizing booster cases, adapters and detonator fuse components for the United States Government as practiced at the International Arms and Fuse Co., of Bloomfield, N. J.

The following solution was here used for a basic deposit:

| | Oz./gal. | g./lit. |
|---|---|---|
| $Zn(CN)_2$ | 6 | 45 |
| NaCN | 6 | 45 |
| NaOH (76 percent) | 2 | 15 |
| $Na_2CO_3$ | 2 | 15 |
| $SnCl_2$ | 1 | 7.5 |

W. R. Barclay, of Birmingham, England,[13] has recommended the following zinc cyanide plating solution:

| | |
|---|---|
| Water | 1 gal. |
| $Zn(CN)_2$ | 10 oz. |
| NaCN | 5 " |
| NaOH | 6 " |
| $Al_2(SO_4)_3$ | 2 " |

W. D. Pleadwell[14] gives the following solution:

| | |
|---|---|
| Water | 1 gal. |
| Proprietary cleaner | 2 oz. |
| Zinc Cyanide | 8 " |
| NaCN (96-98 percent) | 3.5 " |
| NaOH (76 percent) | 7 " |

A review of the above formulas shows that zinc deposits (presumably good) can be obtained from a great variety of zinc cyanide solutions. However, the utter lack of scientific data upon all these baths as regards conductivity, quality of deposits obtained, anode and cathode current efficiency, stability or life of solutions without additions and the relative quality of the anode corrosion makes the choice of the best formula by the commercial plater a game of chance; further than that, the maintenance of any solution he may choose to use is a further problem which is left for his own solution. The need of painstaking research work in this field speaks for itself.

[12] Metal Ind., 1919, **17**, 22-24.
[13] (Institute of Metals), Metal. Ind., 1921. **19**, 159.
[14] Metal Ind., 1921, **19**, 323.

## THE PROPERTIES OF A SUCCESSFUL PLATING SOLUTION.

The vital properties of a commercially successful zinc cyanide plating solution are:

1. It must have high conductivity.

2. It must give a smooth, gray-white, deposit.

3. It must have good anode corrosion (tenacious anode insulating films have been found to ruin the speed of deposition and simultaneously the color of the deposit as well).

4. It must be a fairly stable solution. (The solution should be one which requires a minimum of daily replenishing of salts or it will ultimately foul and become useless due to the high inert salt content. This brings up the entire question of cyanide decomposition).

5. It must have anode and cathode current efficiencies which are as nearly equal as possible.

6. It should have a good "throwing power"; *i.e.,* it should plate irregularly shaped articles with a uniform thickness of zinc throughout.

7. It should give dense, non-porous deposits so as to be as rust resistant as possible for a given thickness of metal.

## OUTLINE OF THE PROBLEM.

Having the above points in view the following series of studies were undertaken:

I. The chemical solubility of zinc in (a) sodium cyanide, (b) sodium hydroxide, (c) sodium carbonate, (d) a sodium zinc cyanide plating solution.

II. The study of the deposits and the anode corrosions obtained from the various types of solution as indicated by the results of I.

III. Studies upon addition agents.

IV. Anode and cathode current efficiencies of the most promising types of solutions as determined by the results of I, II, and III.

V. Studies of the relative throwing power of the zinc cyanide versus the zinc sulphate solution, and upon the relative corrosion

resisting properties of deposits made from (a) cyanide solutions, (b) zinc sulphate solutions, as determined by the salt spray test.[15]

## EXPERIMENTAL.

The grade of the materials which were used in the present research is as follows:

*Anodes:* The anodes used were commercial zinc having the following composition:

| | Percent |
|---|---|
| Copper | 0.65 |
| Lead | 1.31 |
| Tin | 1.65 |
| Iron | 0.12 |
| Zinc (by diff.) | 96.27 |

*Cathodes:* The cathodes used were sheet steel pieces cut from 27 gauge (0.44 mm.) sheets. These were pickled in hydrochloric acid and cleaned in alkali just prior to use.

*Chemicals:* The chemicals used were: sodium cyanide (R. and H. 96-98 percent NaCN content) and zinc cyanide (R. and H. 54.5-55.5 percent zinc content). The remaining chemicals used were Merck's c. p. materials.

### I. DETERMINATION OF CHEMICAL SOLUBILITY OF ZINC IN THE VARIOUS CONDUCTING SOLUTIONS AND IN THE ZINC CYANIDE PLATING SOLUTION.

(See Table I on next page)

*Conclusions:* 1. Sodium cyanide is a better reagent for dissolving zinc than sodium hydroxide; whereas sodium carbonate on the contrary has only a very slight chemical action on zinc.

2. The addition of sodium carbonate to a sodium zinc cyanide solution decreases the solubility of the zinc to about one-half that exerted by the sodium cyanide alone (compare solubilities of solutions 3 and 8).

3. The addition of 3 oz. sodium hydroxide to the sodium cyanide-sodium carbonate solution further decreases the solubility of zinc and brings it down to approximately that of a sodium hydroxide solution (compare solutions 3, 8, and 10).

[15] Circular No. 80 of the Bureau of Standards on "Protective Metallic Coatings for the Rust Proofing of Iron and Steel."

TABLE I.

| No. | Solution Used | Weight of Zinc Dissolved in 12 Hrs. at 50° C. |
|---|---|---|
| 1 | Water—1 gal. ..... Sodium Cyanide—1 oz. ..... | 0.0670 g. The zinc sheet had a gray streaked surface |
| 2 | Water—1 gal. ..... Sodium Cyanide—3 oz. ..... | 0.1310 g. The zinc sheet had a gray streaked surface |
| 3 | Water—1 gal. ..... Sodium Cyanide—7 oz. ..... | 0.2687 g. The zinc sheet had a gray streaked surface |
| 4 | Water—1 gal. ..... Sodium Carbonate—1.5 oz. ..... | 0.0010 g. Zinc sheet surface unchanged |
| 5 | Water—1 gal. ..... Sodium Carbonate—3 oz. ..... | 0.0050 g. Zinc sheet surface unchanged |
| 6 | Water—1 gal. ..... Sodium Carbonate—7 oz. ..... | 0.0050 g. Zinc sheet surface unchanged |
| 7 | Water—1 gal. ..... Sodium Hydroxide—3 oz. ..... | 0.0408 g. Zinc sheet surface was blackened |
| 8 | Water—1 gal. ..... Sodium Cyanide—7 oz. ..... Sodium Carbonate—1.5 oz. ..... | 0.1260 g. Zinc sheet had a gray streaked surface |
| 9 | Water—1 gal. ..... Sodium Cyanide—7 oz. ..... Zinc Cyanide—9.4 oz. ..... | 0.0310 g. Zinc sheet surface unchanged |
| 10 | Water—1 gal. ..... Sodium Cyanide—7 oz. ..... Sodium Hydroxide—3 oz. ..... Sodium Carbonate—1.5 oz. ..... | 0.0476 g. Zinc sheet had a gray streaked surface |

4. These experiments show that the solutions which will have the least chemical action on the anodes are those which have a low free cyanide concentration, and a low sodium hydroxide concentration, and preferably a fairly high carbonate content.

## II. STUDIES OF THE DEPOSITS AND THE ANODE CORROSION OBTAINED FROM THE VARIOUS TYPES OF SOLUTIONS AS INDICATED BY THE RESULTS OF I.

The results of conductivity studies showed that to get a bath having the high conductivity required, the salts tested which

needed to be seriously considered as conducting salts in the zinc cyanide plating solution were sodium hydroxide, sodium cyanide and sodium carbonate. Further, the zinc cyanide solubility studies indicated that the solution should have a low free cyanide content and a high carbonate content and a medium caustic content so as to decrease the chemical solubility of the zinc anodes and simultaneously bring the conductivity of the solution to as high a value as possible.

A long series of plating experiments now carried out in which the concentration of zinc cyanide was varied from 2 to 8 oz. per gal. (15 to 60 g./L.) and in which varying amounts of sodium cyanide, sodium hydroxide and sodium carbonate were tried out. Owing to the general uniformity of the results throughout, and the duplication of the data of the most promising solutions in the work which followed, only the general conclusions obtained are given at this point. These may be summed up as follows:

1. Almost any sodium zinc cyanide solution which contains excess of sodium cyanide will give a smooth, gray-white deposit of zinc on iron cathodes when first made up.

2. Every such solution after a period of electrolysis varying from 1 to 10 hours and usually after about 2 or 3 hours gave only darkened or stained deposits. Usually this stain manifested itself on the middle portion of the cathode. Simultaneously the anodes became badly coated over and the current density dropped to 50 percent of its former value or less.

3. The addition of enough sodium cyanide to again furnish the solution with some free sodium cyanide or the cleaning of the zinc anodes so as to expose a fresh metal surface or the use of sheet iron anodes cause the uniform gray-white deposit to reappear for another period of several hours.

4. The addition of sodium hydroxide even in large amounts did not overcome the stain and it always made the anode coatings worse instead of better. This proves the statement of Langbein[17] that an alkaline zinc solution always causes fouling of the anodes by zinc hydrate. Consequently even though sodium hydroxide is the best conducting salt a high concentration of the same should not be used.

[17] Electrodeposition of Metals, 1914 edition, p. 432.

5. Contrary to the above the addition of enough sodium cyanide so as to leave free sodium cyanide in solution always cleaned the anodes and simultaneously remedied the staining for a duration of time which depended on the amount of sodium cyanide added.

6. We must, therefore, conclude that the success of every zinc cyanide bath depends primarily upon the maintenance of free alkali cyanide in the solution. This is always indexed by the condition of the anodes since free sodium cyanide is the only speedy solvent for the zinc hydroxide anode coating common to alkaline solutions.

7. The addition of sodium carbonate has been found beneficial for the following reasons: (a) It decreases the chemical solubility of the zinc anodes, (b) It decreases the tenacity of zinc hydroxide coatings on the anodes, (c) It increases the conductivity of the solution.[18]

8. As a result of the above conclusions the following approximate concentration of solutions suggests itself for a zinc cyanide plating solution: Zinc cyanide, 4 to 8 oz. per gallon (30 to 60 g./L.), sodium cyanide same quantity as was used of zinc cyanide, sodium hydroxide 1 to 2 oz./gal. (7.5 to 15 g./L.), sodium carbonate 4 oz./gal. (30 g./L.). This bath was tried out and found to give very good results especially when addition agents were added.

## III. STUDIES OF ADDITION AGENTS.

Though the fundamental value of addition agents has been proven almost without exception in acid solutions, no extensive published data were found as to their value in cyanide solutions. The cause for this situation is that in the common cyanide baths, for example, silver, gold, copper and brass, the use of addition agents has not been found necessary. The only common case found is the addition of carbon disulphide or benzol to the silver cyanide solution to give a harder, brighter deposit.[19]

Kern[20] has investigated the effect of gelatine, resorcinol, pyro-

[18] The use of a high carbonate bath containing no caustic suggested itself at this point, but this was tried and found to give only gray colored deposits; the conductivity of the solution also remained somewhat low.

[19] Trans. Am. Electrochem. Soc., 1905, **8**, 83; Metal Ind., March, 1909, p. 96.

[20] Trans. Am. Electrochem. Soc., 1909, **15**, 441.

gallol and tannic acid in plating solutions of silver, copper, and lead. He arrived at the conclusion that "the greater the molecular weight of the addition agent and the larger the number of adjoining hydroxyl and amine radicals which the compound contains, the more effective it is in producing denser, brighter, less crystalline, and more coherent deposits of lead, copper and silver."

Mathers'[21] work agrees in general with this statement.

Among the other theories which have been advanced, the following must be mentioned:

Betts[22] has proposed the theory that the effect of addition agents is due to their reducing action.

Nussbaum[23] has advanced the theory that those colloids are useful which migrate to the cathode, for here they exert a continuously migrating local diaphragm action around the deposit. The colloid automatically travels to the points of highest potential, causing the latter to decrease, thus making the addition agent "a potential stabilizer" at the cathode.

To the present writer it seems probable that all the above factors may come into play at different times and even simultaneously in the case of complex or mixed addition agents. From the above authors' work the following list of addition agents were chosen for trial:

Glucose (corn sugar), gelatine, rosin, lenox soap, sodium benzoate, phenol, gum arabic, gum sandarac, tannic acid, oil of cloves, pyridine, beta naphthol, pepsin, licorice, sodium tartrate; aluminum sulphate, corn sugar and gum arabic combined; and corn sugar, gum arabic and sodium fluoride combined.

*Experimental Procedure.*—The zinc plating solution used in this work consisted of a five-gallon stock solution of the following composition:

| | oz./gal. | g./L. |
|---|---|---|
| Zinc Cyanide ..... | 8 | 60 |
| Sodium Cyanide ..... | 7 | 52.5 |
| Sodium Hydroxide ..... | 6 | 45 |

Temperature of the solution, 48-52° C.

Time of deposition—two 2-hour deposits were made when the results warranted.

Area of anode—9 sq. in. or 58 sq. cm.

[21] Trans. Am. Electrochem. Soc., 1912, **22**, 328.

[22] U. S. Patent No. 713277.

[23] U. S. Patent No. 83202.

Area of cathode—9 sq. in.
Distance between electrodes—1.5 in. or 39 mm.
Current used—1.5 volts.
The volume of solution used for each determination was 300 cc.
The results obtained are given in Table II.

The amount of addition agent used was 0.3 gram. If the deposit was unsatisfactory the amount of the addition agent was then doubled (in the case of aluminum sulphate, sodium fluoride and corn sugar, more was used as is noted in the table below).

*Conclusions:* 1. The following addition agents were found beneficial: Rosin, soap, licorice, gum arabic, gum sandarac, oil of cloves, sodium benzoate, corn syrup and sodium fluoride.

2. Two general types of addition agent effects were observed: (a) The production of a whiter deposit. (b) The production of a very smooth, dense, non-treed deposit.

Rosin, soap, licorice, sodium benzoate, corn sugar, oil of cloves and sodium fluoride produced greater whiteness but gave a rough deposit; on the contrary, gum arabic, gum sandarac and to a lesser extent, oil of cloves, produced greater smoothness of the deposit.

3. It was found that the combined use of gum arabic, corn sugar and sodium fluoride produced both smoothness and a greater whiteness of the deposit, thus combining the two types of addition agent effects.

It is interesting to note that the effect of corn sugar and gum arabic in cyanide solutions has been found to be both of exactly the same kind and equally efficacious in their action on the deposit, as that found by Tainton and Pring[24] in a zinc sulphate bath containing 15 percent of free sulphuric acid.

The marked effect of these addition agents gives further support to the reducing action theory of Betts, especially so in the case of corn sugar; and to the continuously migrating local diaphragm action theory of Nussbaum in the case of gum arabic and gum sandarac.

## IV. THE STUDIES OF THE ANODE-CATHODE CURRENT EFFICIENCIES IN VARIOUS TYPES OF ZINC CYANIDE SOLUTIONS.

The purpose of these determinations was to make a quantitative study of the wide range of zinc cyanide plating solutions in order

[24] Journ. Amer. Chem. Soc., **105**, 710-724.

TABLE II.

| Addition Agent | Weight of Addition Agent Used grams | Kind of Deposit Obtained |
|---|---|---|
| Sodium Tartrate... | 0.3 | Rough—treed—stained |
| | 0.6 | Rough—treed—stained |
| Rosin ..... | 0.3 | The deposit was white, rough and treed for one hour and then staining occurred. |
| | 0.6 | The deposit was white, rough and treed for one hour and then staining occurred. |
| Soap ..... | 0.3 | Rough—treed—slightly stained |
| | 0.6 | Rough—treed—slightly stained |
| Gelatine ..... | 0.3 | Good deposit for 15 min. Thereafter it treed and stained badly. |
| | 0.6 | Treed and stained badly |
| Aluminum Sulphate. | 1.0 | White, rough, many small trees |
| | 2.0 | Dark, rough, badly treed. |
| Gum Arabic ..... | 0.3 | Very smooth, dense, gray-white color |
| | 0.6 | Very smooth, dense, gray-white color |
| Gum Sandarac .... | 0.3 | Very smooth, dense, gray-white color |
| | 0.6 | Very smooth, dense, gray-white color |
| Pyridine ..... | 0.3 | Gray-colored deposit, rough, treed |
| | 0.6 | A stained deposit, rough, badly treed |
| Pepsin ..... | 0.3 | Stained, rough, treed |
| | 0.6 | Stained, rough, treed |
| Tannic Acid ..... | 0.3 | Gray deposit, very rough—treed |
| | 0.6 | Gray deposit, very rough—treed |
| Beta Napthol ..... | 0.3 | Stained—rough—treed |
| | 0.6 | Badly stained—rough—treed |
| Licorice ..... | 0.3 | Slightly stained, rough—treed |
| | 0.6 | Stained—rough—treed |
| Oil of Cloves ..... | 0.3 | A white, smooth deposit for 2 hrs.; thereafter it stained and treed |
| | 0.6 | Stained and treed |
| Sodium Benzoate... | 0.3 | Deposit was white—rough—treed |
| | 0.6 | Stained—non-adherent deposit |
| Corn Sugar ..... | 0.5 | White—rough—treed |
| | 1.0 | White—rough—treed |
| | 2.0 | White—rough—treed |
| Sodium Fluoride ... | 2.0 | White—rough—treed |
| Corn Syrup ..... | 2.0 | Gray-white, smooth, dense deposit |
| Gum Arabic ..... | 0.3 | |
| Corn Syrup ..... | 2.0 | This gave a white deposit which remained smooth and dense and gave the best results of all the addition agents tried. |
| Gum Arabic ..... | 0.3 | |
| Sodium Fluoride... | 2.0 | |

TABLE III.

| Designation | Exp. No. | Comp. of Sol. in Oz./Gal. | | | | Current Efficiency | | Anode Corrosion | Kind of Deposit | Current Density Amp./sq.ft. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $ZnCy_2$ | NaCN | NaOH | Other Salts | Anode Percent | Cathode Percent | | | |
| Morgan | 1 | 8 | 7 | 3 | 1.5 $Na_2CO_3$ | 106 | 56 | Good | Good | 64 |
| Arsenal | 2 | 8 | 7 | 3 | 1.5 " | 105 | 54 | " | " | 64 |
| Formula | 3 | 8 | 7 | 3 | 1.5 " 0.5 $Al_2(SO_4)_3$ | 109 | 68 | " | " | 64 to 40 |
| | 4 | 8 | 7 | 3 | 1.5 " 0.5 " | 105 | 79 | " | Poor | 64 to 40 |
| C. H. Proctor's | 5 | 8 | 7 | 1 | 4 $Na_2SO_4$ 2 NaF | 107 | 42 | Insulating | Poor | 45 to 20 |
| Zinc Sol. | 6 | 8 | 7 | 1 | 4 " 2 " | 91 | 55 | Film | " | 44 to 15 |
| (Stainless) | 7* | 8 | 7 | 1 | 4 " 2 " | 99 | 74 | " | Gray | 27 to 5 |
| Revised | 8† | 8 | 7 | 2 | 4 $Na_2CO_3$ 2 NaF | 101 | 31 | Excellent | Good | 72 to 40 |
| Stainless | 9† | 8 | 7 | 2 | 4 " 2 " | 101 | 55 | " | " | 72 to 40 |
| Zinc Sol. | 10 | 8 | 7 | 2 | 4 " 2 " | 83 | 63 | Fair | Gray&Treed | 40 const. |
| | 11 | 8 | 7 | 2 | 4 " 2 " | 87 | 69 | " | " | 40 to 20 |
| | 12 | 8 | 7 | 8 | ..... | 101 | 93 | Poor | ShinyWhite | 110 |
| | 13 | 8 | 7 | 8 | ..... | 111 | 92 | " | " | 110 |
| High Caustic | 14 | 6 | 6 | 4 | ..... | 106 | 49 | " | Poor | 64 |
| Solution | 15 | 6 | 6 | 4 | ..... | 103 | 42 | " | Spots | 64 |
| | 16 | 4 | 4 | 4 | 4 $Na_2CO_3$ | 99 | 57 | Good | Good | 64 |
| | 17 | 4 | 4 | 4 | 4 " | 108 | 58 | " | " | 64 |
| | 18 | 6 | 6 | 2 | 6 " | 111 | 68 | " | " | 64 |
| | 19 | 6 | 6 | 2 | 6 " | 111 | 70 | " | " | 64 |
| High Carbonate | 20 | 6 | 6 | 2 | 6 " 2 $NH_4OH$ | 111 | 79 | " | " | 50 |
| low caustic | 21 | 6 | 6 | 2 | 6 " 2 " | 104 | 68 | " | Poor | 50 |
| solutions | 22 | 6 | 6 | 2 | 2 " 0.5 " | 110 | 54 | " | Good | 36 |
| | 23 | 6 | 6 | 2 | 2 " 0.5 " | 110 | 49 | " | " | 36 |

* Exp. No. 7 was made using the Stainless Zinc Solution for 9 hours.
† The solution used in Exps. 8 and 9 was now run for 20 hours and tests 10 and 11 were then made with it.

to find the best type of solution to recommend to the zinc plating industry. In addition to the anode-cathode current efficiencies, the kind of anode corrosion, quality of deposit obtained, and relative conductivities of the solutions were observed.

*Experimental Conditions*:

One-half gallon of solution.
Temperature—49 to 51° C.
Area of Anode—16 sq. in. (100 $cm^2$).
Area of cathode—8 sq. in. (50 $cm^2$).
Distance between Anode and Cathode—2½ in. (6 cm.).
Applied E. M. F.—1. 5 volts.
Time of each electrolysis—3 to 4 hours.
The coulometer for measuring the quantity of electricity used in each determination was the nickel-sodium-hydroxide gas coulometer connected in series with the plating bath.
The results obtained are given in Table III.

*Conclusions:* 1. As a result of this work, the revised stainless zinc solution has been found to come the closest to the ideal of any tried out. When made up using sodium fluoride, corn syrup and gum arabic as addition agents, it has been found to give very smooth, non-treed, gray-white deposits. Further, a 112-gallon solution of this kind has now been kept going for four months in the writer's laboratory with uniformly good deposits when the proper additions are made as outlined below. It is, therefore, felt that this solution can be recommended without hesitancy as to its permanent performance in commercial practice. As used, the solution consists of:

| | Oz./gal. | g./L. |
|---|---|---|
| Zinc Cyanide | 8 | 60 |
| Sodium Cyanide | 7 | 52.5 |
| Sodium Hydroxide | 1 to 2 | 7.5 to 15 |
| Sodium Carbonate | 4 | 30 |
| Sodium Fluoride | 1 | 7.5 |
| Corn Sugar | 1 | 7.5 |
| Gum Arabic | ⅛ | 1.1 |
| Temperature of Solution | 40-50° C. | .... |
| Voltage | 3 to 5* | .... |

* Depending on the amount of work to be plated.

The maintenance of the above solution is primarily a question of keeping a small amount of free alkali cyanide in the solution at all times. Now since the zinc anodes slowly neutralize the free alkali cyanide chemically, especially when the solution is not in use, the frequent addition of small quantities of sodium cyanide

is the essential factor. The situation here is similar to that in the zinc sulphate solution to which daily additions of sulphuric acid must be made to keep up the acidity of the bath. The additions of zinc cyanide should be made as analysis indicates. Roughly, this usually is about ¼-½ that of the sodium cyanide added and will vary with the drag-out the solution may undergo.

The only other additions of importance necessary are the occasional replenishing of the addition agents, sodium fluoride, corn sugar and gum arabic. In practice, two stock solutions should be made up, the former containing sodium and zinc cyanide and the latter, the three addition agents in the proportions given in the formula. The solution should then be maintained by the frequent addition of the cyanide as shown to be necessary by analysis and an occasional replenishing of the addition agents as the color of the deposit may indicate.

2. The fundamental factors in a zinc cyanide solution have been found to be:

*A.* The anode and cathode current efficiencies.

*B.* Good anode corrosion.

*C.* The color and smoothness of the deposit.

*D.* The conductivity of the solution.

*E.* Stability or life of the solution without additions.

*A. The Results of Current Efficiency Studies:*

(a) Cathode current efficiencies in zinc cyanide solutions giving good deposits are usually somewhat low (50 to 75 percent), while the anode efficiencies are high (90 to 110 percent). The only exceptions to the above statements are found in the high caustic solutions, experiments Nos. 12 and 13 and to a lesser extent in the revised stainless zinc solution, in which the anode and cathode current efficiencies are more nearly equal. The low cathode current efficiency, however, is not detrimental, but beneficial, since the hydrogen evolved is an excellent electric cleaner which is a very necessary factor in almost all commercial zinc plating practice.

(b) The cathode current efficiencies are inversely dependent upon the concentration of the free alkali cyanide and fall very rapidly as the concentration of the latter is increased.

*B. Anode Corrosion:*

(a) Good anode corrosions (by this we mean such a corrosion as will not foul the anodes so as to electrically insulate them) are directly dependent upon the concentration of the free alkali cyanide in the solution and to a lesser extent upon the anode impurities such as copper, lead, etc.

(b) Since a good anode corrosion and a fairly high cathode current efficiency are both essential in a successful zinc plating solution, the free alkali cyanide content should have the lowest value which good anode corrosion will allow. In practice, as long as appreciable quantities of free cyanide exist, good anode corrosion is assured.

*C. Quality and Color of the Zinc Deposit:*

The quality and color of the zinc cyanide deposits depend first and foremost upon the presence of free alkali cyanide in the solution, *i. e.*, the zinc in the solution must exist there very largely as sodium zinc cyanide. This situation is possible only when the sodium hydroxide concentration is low, so as to prevent the formation of sodium zincate by suppressing the reaction:

$$Na_2Zn(CN)_4 + 4NaOH \leftrightarrows Na_2ZnO_2 + 4NaCN + 2H_2O.$$

To expect a uniform quality of cyanide zinc deposit from a solution containing much free sodium hydroxide, and, consequently, some sodium zincate, is just as illogical as it would be to expect zinc and copper to plate uniformly, *i. e.*, to give a brass deposit from an acid solution; for zinc is deposited from the zincate solution at 0.5 volt, whereas it requires 2.5 volts to deposit it from a cyanide solution. Any considerable amount of zincate in the solution would, therefore, mean that the zinc would be deposited from that compound entirely and not at all from the cyanide compound. Thus what we obtain from a high caustic solution is essentially a zincate zinc deposit and not a cyanide zinc deposit at all.

Now, while zinc can be deposited from a sodium hydroxide-sodium zincate solution, the commercial deposition of zinc from such solutions has always given badly stained deposits which have made this type of solution a failure in practice. In exactly analogous manner, the use of a high sodium hydroxide concentration in

the zinc cyanide plating solution has made it a failure where uniform gray-white deposits were essential to the success of the solution. The deposits from high-caustic cyanide solutions after the bath has operated a few hours, are always stained and look exactly like deposits from sodium hydroxide-sodium zincate solutions. The writer believes that the stained deposits of the high caustic cyanide solution actually come from the zincate there present. Experiments on cathode single potentials are planned to determine whether the cathode potential obtaining when these stained deposits occur are essentially those of the zincate solution or not.

In harmony with this view, we have in a large series of experiments always found that high caustic zinc cyanide plating solutions invariably give stained deposits and, further, that the degree of staining is roughly proportional to the concentration of the caustic in the solution. The maximum amount of caustic soda which has been found can be successfully counteracted by addition agents, as far as staining is concerned, is 2 oz. per gallon. Even then the deposit has a slightly darker color than when the caustic is down to one ounce per gallon. Two ounces per gallon of sodium hydroxide is therefore the maximum amount which can be successfully used when the color of the deposit is important.

*D. Conductivity of the Solution:*

The vital necessity in any electro galvanizing solution is that it shall possess a high conductivity so as to allow the maximum quantity production. Since sodium hydroxide gives the zinc cyanide solution a very high conductivity temporarily, the usual practice among platers when the conductivity falls is to add caustic to the solution. Temporary success, due to the liberated sodium cyanide followed by subsequent decreased conductivity to the value obtaining prior to the addition, invariably results. Simultaneously, stained deposits are obtained. The primary cause for this situation lies in the badly insulating zinc hydroxide anode coating which invariably is produced by a high caustic solution. The true remedy for increasing the conductivity in such an anode insulated solution consists in adding sodium cyanide, thereby cleaning the anodes of their hydroxide coating and restoring the zinc cyanide content of the solution.

In the revised stainless zinc solution, the anode insulation is prevented by keeping the caustic low and substituting sodium carbonate as the conducting salt, thereby preventing the anode insulation, and thus eliminating the chief source of trouble as regards the conductivity of the cyanide solution.

*E. Stability of Life of the Solution:*

The life of the cyanide zinc solution depends primarily upon the stability of the cyanides present. Since cyanides decompose considerably by hydrolysis at highly elevated temperatures, the temperature of the bath should not be allowed to rise above 60° C. (140° F.) and preferably should be kept at about 50° C. (122° F.). Under these conditions only a slight decomposition takes place and the life of the solution is well maintained.

## V. STUDIES OF THE COMPARATIVE THROWING POWER OF CYANIDES VS. SULPHATE ZINC SOLUTIONS; AND OF THE COMPARATIVE RUST-RESISTING PROPERTIES OF CYANIDE VS. SULPHATE ZINC DEPOSITS AS INDEXED BY THE SALT SPRAY TESTS.[25]

Though the data which follow are only partially complete, the uniform agreement of the tests made warrant their inclusion at this time, since the evidence is clean-cut and in harmony with that found by earlier workers[26] and generally admitted in the zinc plating industry.

*Experimental:* The zinc plating solutions used for these tests had the following compositions:

| A. *Zinc Cyanide Solution* | Oz./gal. | g./L. |
|---|---|---|
| Zinc Cyanide | 6 | 45 |
| Sodium Cyanide | 6 | 45 |
| Sodium Hydroxide | 2 | 15 |
| Sodium Carbonate | 6 | 45 |
| Sodium Fluoride | 2 | 15 |
| Corn Sugar | 1 | 7.5 |
| Gum Arabic | ⅛ | 1 |

Temperature of electrolysis, 50° C.
Voltage, 5 volts.
Current density, 40 amp./sq. ft. (4.4 amp./sq. dm.) when area of anode surface : cathode surface : : 3 : 1.

[25] Cir. Bureau of Standards No. 80, Protective Metallic Coatings for the Rust Proofing of Iron and Steel.

[26] *Ibid.*, pp. 7 and 17.

| B. *Sulphate Solution* | Oz./gal. | g./L. |
|---|---|---|
| $ZnSO_4.7H_2O$ ..... | 22 | 165 |
| $H_2SO_4$ ..... | ¼ to ⅛ | 2 to 1 |
| Corn Sugar ..... | 1.7 | 12.5 |
| Licorice ..... | ⅓ | 2.5 |

Temperature of electrolysis, 25° C.
Voltage, 5 volts
Current density, 20 to 25 amp./sq. ft. (2.2 to 2.75 amp./sq. dm.) when area of anode surface : cathode surface : : 3 : 1.

This solution was made up the same as it is made in standard commercial zinc plating practice. Sixteen ounces $ZnSO_4.7H_2O$ were dissolved in ¾ gallon of water. The sulphate equivalent of 6 ounces $ZnSO_4.7H_2O$, of sulphuric acid was then added together with 1⅔ ounces corn sugar and ⅓ ounce of licorice. Zinc anodes were now put into the solution and it was then left to work for 12 hours. The solution was now made up to one gallon, 10 cc. of acid added and it was then ready for use.

Two deposits were made at one time, one being used for the Cushman test to determine the amount of zinc deposited per square foot of surface, while the other was put into the salt spray test. By this method the time of rusting of different amounts of zinc was determined in each type of solution. The experimental data obtained are given in tabular form in Table IV.

### CONCLUSIONS FROM THE CUSHMAN AND SALT SPRAY TESTS.

1. Zinc deposits of about 1/10 ounce per square foot (0.3 g/dm²) of zinc from a cyanide deposit are amply sufficient to withstand a 40-hour salt spray test. On the other hand, the sulphate solution requires a deposit ranging somewhere between 0.12 and 0.24 ounce per square foot (0.36 to 0.72 g./dm²). For safety, when plating under definite specifications, this would have to be 0.2 ounce per square foot. The causes for this very marked increased rust resisting property of the cyanide deposits which are responsible for this wide difference are:

(a) The iron under a cyanide zinc deposit is coated with more or less of a film of an alkaline solution, and this alkali protects the iron by keeping it passive; whereas in the sulphate solution, the acid film tends to stimulate rusting of the underlying iron.

## TABLE IV.

### *Rust Resistance of Deposits.*

| Article Plated | Time Plated Min. | Hydrogen evolved in cc. corrected to 0°C & 760 mm. | Area stripped by acid by Cushman test* Sq. In. | Oz. Zinc per Sq. Ft. | Time required to produce rusting in salt spray apparatus Hours |
|---|---|---|---|---|---|
| *A. Cyanide Zinc Deposits.* | | | | | |
| 4 x 6 in. iron sheet. | 10 | 121 | 24 | 0.074 | 42 |
| 4 x 6 in. iron sheet. | 10 | 108 | 24 | 0.066 | 42 |
| 4 x 6 in. iron sheet. | 10 | 112 | 24 | 0.068 | 42 |
| 4 x 6 in. iron sheet. | 20 | 287 | 24 | 0.177 | 128 |
| 4 x 6 in. iron sheet. | 20 | 310 | 24 | 0.190 | 128 |
| 9 in. section of Hayes' clincher rim..... | 10 | 14.2† | 1.917 | 0.109 | 48 |
| | | 11.1‡ | 1.917 | 0.086 | |
| | | 15.1¶ | 3.517 | 0.064 | |
| 9 in. section of Hayes' clincher rim..... | 10 | 13.8† | 1.917 | 0.106 | 48 |
| | | 9.8‡ | 1.917 | 0.075 | |
| | | 14.7¶ | 3.517 | 0.062 | |
| 9 in. section of Hayes' clincher rim..... | 20 | 35† | 1.917 | 0.240 | 180 |
| | | 37‡ | 1.917 | 0.254 | |
| | | 47¶ | 3.517 | 0.176 | |
| 9 in. section of Hayes' clincher rim..... | 20 | 35.5† | 1.917 | 0.243 | 180 |
| | | 33.0‡ | 1.917 | 0.226 | |
| | | 45.5¶ | 3.517 | 0.171 | |
| *B. Sulphate Zinc Deposits* | | | | | |
| 4 x 6 in. iron sheet. | 10 | 191 | 24 | 0.1176 | 16 |
| 4 x 6 in. iron sheet. | 10 | 199 | 24 | 0.1220 | 16 |
| 4 x 6 in. iron sheet. | 20 | 452 | 24 | 0.2780 | 60 |
| 4 x 6 in. iron sheet. | 20 | 402 | 24 | 0.2470 | 60 |
| 9 in. section of Hayes' clincher rim..... | 10 | 16.9† | 1.917 | 0.130 | 16 |
| | | 8.9‡ | 1.917 | 0.068 | |
| | | 13.4¶ | 3.517 | 0.056 | |
| 9 in. section of Hayes' clincher rim..... | 10 | 14.5† | 1.917 | 0.112 | 16 |
| | | 10.4‡ | 1.917 | 0.080 | |
| | | 13.3¶ | 3.517 | 0.057 | |
| 9 in. section of Hayes' clincher rim..... | 20 | 16.0† | 1.917 | 0.123 | 64 |
| | | 17.4‡ | 1.917 | 0.134 | |
| | | 18.8¶ | 3.517 | 0.079 | |
| 9 in. section of Hayes' clincher rim..... | 20 | 16.9† | 1.917 | 0.130 | 72 |
| | | 16.5‡ | 1.917 | 0.127 | |
| | | 20.5¶ | 3.517 | 0.089 | |

* Cushman, U. S. Pat. 1,372,405. † Outside. ‡ Tireside. ¶ Under Clinch.

(b) The cyanide bath gives a more non-porous deposit than the sulphate bath, which roughens very rapidly.

(c) The cyanide bath is a cleaning as well as a plating bath, and therefore covers the metal completely with zinc, even though the iron may be only partially clean, whereas the acid solution under poor cleaning conditions at once fails to plate the unclean parts. In practice most iron is heavily covered with grease and is very frequently not entirely clean when plated. The cyanide plating solution requires less careful cleaning of the work than the sulphate solution, for which the grease must be removed by burning it off.

2. The ratio of zinc deposited on the exposed surface of a tire rim to that under the clinch is about 1:0.71 from the cyanide solution, whereas in the sulphate solution, this ratio is about 1:0.45. In the case of the edge and the groove of the threads on bolts, this ratio has been found by the Bureau of Standards[27] to be about 1:0.25, presumably in a sulphate zinc solution. To get a given amount of zinc under the clinch in a zinc sulphate solution more than double that amount must be deposited on exposed surfaces; and for rims where the exposed surface is far in excess this means that almost two times as much zinc must be deposited so as to protect the recessed portions.

3. The specifications of a given amount of zinc per square foot of surface is unscientific, and should be changed in practice to a salt spray test requirement in all commercial plating fields where corrosion resistance is the aim, since this test comes the closest to indicating the truly protective properties of the plated ware.

4. The superiority of the cyanide over the sulphate deposits as a rust proofing coating has been convincingly proven.

The author wishes to express his appreciation to Dr. Sterling Temple, Mr. M. E. Stewart and Mr. C. H. Proctor for the helpful suggestions they have made while carrying out this work.

[27] Bureau of Standards Circular No. 80, "Protective Metallic Coatings for the Rust Proofing of Iron and Steel."

## DISCUSSION.

WM. BLUM[1]: A few years ago the Bureau of Standards conducted some experiments, admittedly preliminary, on zinc cyanide plating solutions, the results of which have been summarized in Bureau of Standards Technologic Paper 195. The differences between our results and those reported by Mr. Wernlund, emphasize the need for a more exhaustive study of the subject.

With the solutions and anodes used by us we found the presence of considerable amounts of alkali was beneficial, and of carbonate was detrimental, whereas Mr. Wernlund, with his solutions and anodes, reached the opposite conclusions. One reason for these apparent discrepancies is that we worked under different conditions. Our solutions were prepared in all cases by the solution of zinc oxide in sodium cyanide, a procedure recommended at a time when it was especially desirable to conserve the more expensive "metal cyanides." These solutions therefore necessarily contained a large amount of alkali, liberated by the solution of the zinc oxide. Mr. Wernlund's solutions were prepared principally from zinc cyanide and sodium cyanide, and contained no free alkali unless it was added subsequently.

Another marked difference in procedure was that we used for anodes zinc of high purity, while the zinc used by Mr. Wernlund contained appreciable amounts of other metals. These impurities may be in part responsible for the discolored deposits secured by him. Wherever available the use of pure zinc anodes is desirable, as the protective value of pure deposits is no doubt greater.

It is unfortunate that the author has recommended the use of several addition agents, as the resultant solution is so complicated that it could not be controlled by chemical analysis. As the purpose of zinc plating is for protection and not for ornament, the appearance should not be so important as the quality.

For the reasons given by Mr. Wernlund, pure zinc deposits from the cyanide solution may furnish better protection than those from the sulphate. It is probable, however, that in the former

[1] Chemist, Bureau of Standards, Washington, D. C.

solutions, impurities are more likely to be carried over into the deposit than in the sulphate. In the latter solutions there is a greater difference in potential between zinc, copper and lead than in the cyanide solutions.

The subject of "throwing power," to which Mr. Wernlund has referred, is greatly in need of study to define the determining factors, and thus to control this property.

C. H. PROCTOR[2]: We know that the amount of zinc deposited is still a factor, and in commercial practice the deposit must be white. The cleaner and better looking the coating the more salable it is.

WM. BLUM: They ought to be educated.

C. H. PROCTOR: The amount of zinc deposited is still an important factor, as is the uniformity of deposition over the entire rim.

Accordingly, we have to consider in zinc plating not only the amount of metal deposited, but also the finish that is produced. We must have an absolutely smooth, clear surface to meet commercial demands. I ought to make another statement. Dr. Blum spoke about polarization; I realize that cyanide solutions have limitations, but I believe those limitations have been reached. I am not going to make any statement at this time, but I would like to ask Dr. Blum whether they have succeeded in plating cast iron or steel that is high in carbon? I myself have not succeeded with cyanide solutions, but I am going to say frankly that it can be done, and I would like to know if Dr. Blum has any idea why you cannot deposit zinc on cast iron from cyanide solutions.

If we say polarization is the cause, then is it not possible that we can make an addition to a solution that would act as a depolarizer? Frequently there are commercial metals that we cannot plate directly upon, but if we immerse them in diluted nitric acid, the surface becomes passive and it is then possible to plate them. The passivity produced upon cast iron with nitric acid disappears in a moment. What can we add to cyanide solutions that will overcome that difficulty in zinc plating? While we say the staining does not amount to anything, it confronts us in commercial practice, when manufacturers try to sell their products. You cannot sell

[2] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chemical Co., New York City.

a stained article to a purchasing agent because the finish does not appeal to the eye.

C. J. WERNLUND: I fully agree with Dr. Blum that a high concentration of caustic soda in the zinc cyanide solution gives finer grained, non-porous deposits. But, in practice, we have, to our dismay, found that high caustic soda solutions always gave dirty, gray-colored and stained deposits, which were hopeless, commercially. The joker is that high caustic soda solutions usually start out by giving fine deposits, and about the time you have shaken hands with yourself two or three times the staining begins, usually the second or third day. Once this staining manifests itself, it recurs daily, and usually after the bath has been operated for five or six hours. The addition of further caustic soda and cyanides, together with rest periods, usually gives temporary relief, but gradually the staining gets worse, until finally only one remedy remains, which is to throw a part of the solution down the sewer and dilute the remainder.

The speaker has had a plant, using zinc cyanide solutions, under close observation for several months, and every solution which carried from six to ten oz./gal. (45 to 75 g. per L.) of sodium hydroxide forced the plater to resort to just this "cutting down" treatment. On the other hand, those solutions which carried less than four oz./gal. (30 g. per L.) of sodium hydroxide always responded well when the sodium zinc cyanide stock solution was added, and gave a uniform, high quality deposit. Thus practical experience has shown us that the use of high caustic soda solutions invariably leads to endless trouble and waste and therefore should be avoided.

Since we were forced to abandon high caustic soda solutions, we utilized the best substitute for some of the caustic soda we could find, namely, soda ash. We overcame the poorer quality of the deposit by using a little gum arabic, corn syrup and sodium fluoride, and succeeded in making a zinc deposit one inch thick and weighing over 20 pounds without any difficulty. In fact this deposit was a "by-product," in that it was plated nights and during periods when the tank was not required for other work.

Dr. Blum's criticism concerning the use of the impure zinc anodes is what we expect from his Bureau. The use of only

the purest zinc for anodes is to be highly recommended. However we usually find our customers stocked up with several months or a year's supply of the cheaper "prime western spelter" anodes, which usually run around 98 percent zinc, and contain appreciable quantities of lead, arsenic, tin, cadmium, etc. Such being the status of the industry, the plater wants a solution which will work with the anodes he has in stock; and in order to duplicate experimentally what is almost invariably found in practice we chose the impure "prime western spelter" for this work.

In order to make our position perfectly clear, we wish to state that we recommend the use of the highest grade of anodes and of chemicals available, since this makes the quality of the work better and lessens the difficulty of control of the solution.

COLIN G. FINK[3]: In that connection I would like to ask Dr. Blum what anode efficiencies were obtained with pure spelter anodes?

WM. BLUM: I cannot give exact figures, but I know that the anode efficiencies are in practically every case 100 percent or slightly above.

COLIN G. FINK: I gathered from what Mr. Wernlund said that the anode efficiencies were 110 percent with the impure anodes. This ten percent "over efficiency" was largely due to local couples, due to impurities in the anodes.

C. J. WERNLUND: These anode-cathode efficiency determinations were made with clean anodes. It has been found in practice in electrolyses covering several days that the anode efficiency, instead of being 105 or 106 percent, drops down to that of the cathode, and in many cases drops below it.

J. W. RICHARDS[4]: It might be possible, if there is a large demand for very pure anodes, that the makers of electrolytic zinc could deposit their cathodes in a form that could be used as anodes, thus obviating the re-melting of the zinc. You would then get purer metal than you can possibly get in zinc that is re-melted, because the re-melting operation brings in impurities.

I am not an expert plater, but my impression is that the throw-

[3] Consulting Electrometallurgist, New York City.
[4] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

ing power or ability to plate in the interstices depends upon two factors, (1) a high concentration of the metal to be deposited, and (2), a high conductivity of the solution.

WM. BLUM: Apparently other factors may determine the throwing power. A zinc cyanide solution with a low content of zinc will throw better than a sulphate solution with high zinc content. The conductivity has some effect, but probably the throwing power is determined principally by the metal ion concentration, and the polarization characteristics of the solution.

C. S. WITHERELL[5]: Has not the distance between the electrodes something to do with it?

WM. BLUM: Oh yes, we were speaking of the throwing power at a given distance.

J. W. RICHARDS: I was speaking of the throwing power in solutions of the same nature. I got better throwing power in the interstices with concentrated than with more dilute solutions.

G. B. HOGABOOM[6]: This paper offers a solution that is a step backwards in electroplating. Electroplaters, as a rule, are striving to obtain solutions which can be controlled by analysis. With such a complex solution as given that would be almost an impossibility.

Exception is taken to the statement that it is essential to have an electroplating solution that will clean the work. The almost universal practice is to clean the work before putting it into the plating solution; the only exception known is when for some classes of work a cleaning and plating solution such as recommended by Dr. O. P. Watts[7] is used.

Commercial zinc generally contains lead which is a very bad impurity in anodes used for zinc solutions, as it does not go into solution and will foul the anodes. The highest grade sodium cyanide is recommended, yet the very impurities which are commonly found in sodium cyanide of lower grade are added. Why not use the most economical, if the same composition of solution is obtained?

[5] Metallurgical Enginer, New York City.

[6] Research Electroplater, Scovill Mfg. Co., Waterbury, Conn.

[7] Cleaning and Plating in the Same Solution, O. P. Watts, Trans. Am. Electrochem. Soc., 1915, **27**, 141.

C. J. WERNLUND: I would like to ask in regard to the caustic content. Did it cause a decrease or an increase in conductivity?

G. B. HOGABOOM: The lack of sodium hydroxide causes the anode to become coated and that acts as a polarizer.

C. J. WERNLUND: You mean that increasing the caustic content increased the conductivity?

G. B. HOGABOOM: It is doubted whether "conducting salts" is the right term. It is used too broadly. A salt that may increase the conductivity of a solution does not necessarily dissolve the product formed at the anode during electrolysis. The sodium hydroxide, in this particular case, was not added as a "conducting salt," but to dissolve the product formed at the anode and thereby keep the anode clean so that there would be a better passage of the current.

C. J. WERNLUND: In other words, a reducing agent.

G. B. HOGABOOM: No, a dissolving agent that would take into solution that which was formed at the anode.

W. E. HUGHES[8] (*Communicated*): Mr. Wernlund's paper on the zinc plating solution is a valuable one. It incorporates the results obtained in a serious attempt to deal with a difficult problem, namely, deposition from an alkaline plating bath. Many of the facts disclosed in the paper contribute much to present knowledge of such baths. But several of the conclusions which the author has drawn from his results are, it is suggested, open to grave objection. Among them are the author's conclusions from the Cushman and salt spray tests.

The author attributes the increased rust-resisting property of the cyanide deposits, as compared with acid bath deposits, to three causes: 1 (a). Under this sub-heading, he says that the iron under the cyanide zinc deposit is coated "with more or less of a film of alkaline solution," which renders the iron passive and so protects it. This statement has no support at all from the author's own experiments, and it is believed that there is no support for it to be found in the literature. It has, indeed, been shown that iron immersed in caustic alkali rusts more slowly than in

[8] Electrometallurgist, London, England.

solutions of salts and acids (*v* J. N. Friend, Corrosion of Iron and Steel, Chaps. 8 and 9) ; but that is a different matter. There is no justification at all for the jump from simple alkaline solution to a complex solution such as an alkaline plating bath. Moreover, it is assumed by the author that there is more or less of a film of solution coating the iron and under the zinc deposit. The author gives no proof of this. If he could prove the existence of any such film, he would show at the same time that there was no true adherence or coherence between the iron and the zinc; and, further, the author's own results show that such a film, if it were there, would be destructive of the zinc deposit from the inside.

1 (b). Another cause, given by the author for the better protection he finds deposits from the cyanide bath to give the subjacent iron, is that the cyanide bath gives a more non-porous deposit than the sulphate bath. In this regard, my experimental results are contrary to those of the author. I have examined under the microscope deposits of zinc formed in all kinds of solutions, and I find that deposits from acid baths of suitable composition and formed under proper deposition conditions are at least equally close-grained and free from inter-granular interstices, cracks, and so on, as are deposits from cyanide baths. I have recently published micrographs (Beama, Oct., 1921, Figs. 4 and 5) that show beyond doubt how close and fine-grained deposits from the sulphate bath may be. Deposits from cyanide baths, whether copper, brass, or other metal, are known to possess, usually, a structure of fine grain, and to be what is vaguely called "dense." But it does not follow that the structures of deposits from sulphate baths may not be just as satisfactory, from the plating point of view, and, thus, be just as little porous. The author has no real ground for making the general, comparative, deduction he has drawn.

1 (c). In this sub-section, the author gives, as a reason for the preference for cyanide zinc-plating baths, the fact that "the cyanide bath is a cleaning as well as a plating bath," and the further reason that "the cyanide plating solution requires less careful cleaning of the work than the sulphate solution." My view is that in such advocacy the author has done the art of electroplating a distinct dis-service. He is, in effect, telling the

man in the shop that, if he uses the cyanide bath, he need not trouble to clean his work properly; the solution will do it for him. Now, cleanliness in the plating shop should be almost a religion. In many years' workshop experience I have found that more troubles arise from dirty workmanship than from all other causes put together, and I count it as one of my successes in life that I was principally responsible for stopping the spreading of the use of so-called "cleaning and plating" baths. It needs but a moment's thought to see that such baths cannot work for any length of time; the impurities that quickly accumulate in the bath see to that. Their employment cannot for a moment be encouraged. They militate against all the best canons of plating shop practice. It is regrettable indeed that Mr. Wernlund should have lent any countenance to such practice.

There are many other statements and conclusions in Mr. Wernlund's paper that will not bear close scrutiny. I will mention only one other. The author's final conclusion (No. 4) is that "the superiority of the cyanide over the sulphate deposits as a rust proofing coating has been convincingly proven." My view is that, with such facts in mind as those pointed out above, a competent man would be far from convinced that the author had proved anything of the kind. The truth is that while the experimental work of the author is valuable, and will be useful to those engaged in work on electro-galvanizing, whether in the laboratory or workshop, the deductions that he has drawn from those experimental facts are, many of them, wholly unwarranted.

A. G. Betts[9] (*Communicated*): Mr. Wernlund's careful and thorough work should be of great value in the electroplating of this important metal, zinc. He brings out, however, that a careful balance of the sodium cyanide is necessary to get results, and that a large excess of cyanide must be avoided, in order to keep down direct chemical action on the electrodes. In this connection, it would seem that it would have been worth while to use chemically pure zinc anodes, or at least anodes of electrolytic zinc, which certainly is far less active chemically in acid electrolytes, and could well be so, in the cyanide solution. If the parallel should be found to hold, the rate of anode solution and that of cathode

[9] Chemist and Engineer, Hot Springs, N. C.

deposition could be brought much closer together, with the obvious advantages.

Mr. Wernlund discusses the desirability of caustic soda to increase conductivity, but shows the impracticability of this means for the purpose. Theory would indicate that sodium chloride would be better than caustic soda, and that in presence of sodium chloride the anode action would be better. In the presence of sodium choride, the zinc would go into solution primarily as zinc chloride, and the tendency toward the formation of insoluble coatings on the anodes, and the necessity of maintaining chemical means to dissolve the coatings, would be largely or entirely eliminated, beside the increase in conductivity.

Mr. Wernlund follows previous authors in the use of the term "addition" agents which seems to be quite meaningless and lame. Ordinarily, we speak of "oxidation," "decolorizing," etc., agents with reference to a property or function which is understood or known, but this term would be difficult to classify, and if it conveys any knowledge or idea it certainly is not apparent what such idea is, unless it may be something in arithmetic.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, October 1, 1921, President Acheson Smith in the Chair.*

# THE ELECTRODEPOSITION OF LEAD-TIN ALLOYS.[1]

By W. Blum[2] and H. E. Haring[3]

## Abstract.

It is possible to deposit from fluorborate solutions alloys of lead and tin, which are finer grained than either of the metals deposited under similar conditions. Lead and tin can each displace the other from such solutions, until an equilibrium is reached, at which the two metals have the same potential. During continued electrolysis with lead-tin anodes, of solutions containing lead and tin, the ratio of the metals in the deposit always tends to approach that in the equilibrium solution. The process is used on a commercial scale by the Navy Department.

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## I: Introduction.

In the effort to find a satisfactory metallic coating for the inside of air-flasks of naval torpedoes, Mr. James S. Groff, Chief Chemist of the Naval Torpedo Station at Newport, Rhode Island, discovered that it is possible to deposit electrolytically from either fluoborate or fluosilicate solutions an alloy of about 50 percent lead and 50 percent tin which has the desired properties. This process, which has been patented by Mr. Groff[4] is now used successfully for the above purpose by the Navy Department. At the request of that department, the Bureau of Standards conducted an investigation to determine the most favorable conditions of operation, the results of which are reported in this paper. Entirely apart from the possible commercial applications of lead-

[1] Manuscript received August 22, 1921. Published by permission of the Director of the Bureau of Standards and of the Chief of the Bureau of Ordnance, Navy Department.

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[4] U. S. Patent 1,364,051; Dec. 28, 1920.

tin plating, the subject proved to be a favorable example of alloy deposition, owing to the fact that the cathode efficiencies are nearly one hundred percent, and in consequence the solutions do not change much during normal operation. Because of this fact the study was less complicated than would be that of brass plating, a much more commonly used process, in which the cyanide solutions are subject to change during operation.

## II: METHOD IN COMMERCIAL USE.

The method originally used by the Navy Department is essentially as follows: A lead fluoborate solution similar to that used in lead plating[5] is prepared, and is electrolyzed with "dummy" cathodes and with anodes containing 50 percent lead and 50 percent tin. The cathode deposit, which at first consists of pure lead, increases in tin content until it reaches that of the anodes, when the solution is ready for regular operation. (During this investigation it has been shown that the same result can be reached more quickly by the use of tin anodes until the desired cathode composition is secured. This method is now used by the Navy Department). During operation the solution is agitated by means of compressed air. A current density of about 7 amp./sq. ft. (0.8 amp./sq. dm.) is employed and deposition is continued until a thickness of from 0.003 to 0.006 inch (0.075 to 0.15 mm.) is secured.

Deposits so produced are very fine grained and smooth, and have yielded excellent service in the air-flasks, and on torpedo fittings, where their function is to protect the steel against corrosion. Apparently the deposits are sufficiently flexible to remain adherent in spite of the expanding of the steel when subjected to air pressure.

So far as known, the process has not been applied except for the above purpose. Any protection which the deposits afford against corrosion of steel must be due to their very fine structure and impermeability, and not to any intrinsic protective action such as is exerted by zinc. On the other hand the presence of the tin makes the deposits less resistant to the action of acids

[5] "Lead Plating from Fluoborate Solutions," W. Blum, F. J. Liscomb, Z. Jencks and W. E. Bailey. Trans. Amer. Electrochem. Soc., 1919, 36, 243.

than are lead deposits, hence they are not a substitute for lead coatings.

### III: PRINCIPLES INVOLVED IN ALLOY DEPOSITION.

In order that two metals may be deposited simultaneously and continuously from a solution, it is necessary (a) that their potentials in the solution concerned be very close to each other, or (b) that through depolarization by one of the metals, the equilibrium discharge potential of the other metal is altered sufficiently to make it practically equal to that of the first metal. Such a depolarizing action involves the formation at the cathode of an alloy in which the metals are present either as a solid solution or as a compound. Similarly, in order for two metals to go into solution completely and continuously from an anode, their potentials must be very close together, or the anode must consist of a solid solution or a chemical compound.

As will be shown in this paper a deposit consisting of two metals may have a much finer crystalline structure than that of either of the component metals when deposited under similar conditions. This fact probably accounts in part for the lack of data upon the actual internal structure of electrodeposited alloys. In the present case a few attempts were made[6] to study the structure of the deposited lead-tin alloys, but partly because of the difficulty of polishing and etching these soft metals, no definite orientation could be observed. In the absence of such evidence it is difficult to state whether the deposits were true alloys, or simply intimate mixtures of the two metals. As, however, in the lead-tin system there are no compounds and only a limited range of solid solutions, this system is not especially favorable for a study of the structure of electrodeposited alloys. Probably a more critical study of the electrolytic potentials in this and other systems than was possible in this investigation, will throw light upon this point.

Lead-tin alloys prepared by fusion have according to Rosenhain and Tucker[7] a eutectic point which corresponds with 62.9 percent tin by weight or 74.6 atomic percent of tin. At the eutectic temperature lead dissolves about 16 percent of tin but

[6] By H. S. Rawdon of this Bureau.

[7] Phil. Trans. Royal Soc., London, 1909, **209**, A. 89.

since the tin separates in a nearly pure state on cooling, we may assume that the solid alloys consist essentially of tin and a solid solution of tin in lead containing approximately 9 percent of tin. This solid solution probably has a potential very close to that of pure lead. When such alloys are used as anodes we are therefore concerned essentially with the potential of lead and tin respectively in the particular solution. In those solutions in which tin and lead have practically the same potential, the lead-tin anode will dissolve as if it consisted of one metal.

The problem therefore resolved itself into (a) the determination of the conditions under which lead and tin have equal potentials in fluoborate solutions, and (b) the relation between the ratio of the two metals in the solution and in the deposit obtained from it under any given conditions. From such data it should be possible to define the favorable conditions for the production of a deposit of desired composition, and to predict the effect of any change in such conditions.

## IV: PREPARATION AND ANALYSIS OF SOLUTIONS AND DEPOSITS.

### *Lead Fluoborate.*

Lead fluoborate solutions were prepared as described in the paper upon lead plating[8] above referred to. It was found most convenient to employ throughout (unless otherwise stated) solutions in which the total metal content was $N$, the total fluoboric acid ($HBF_4$) was 1.5 $N$ and the excess of boric acid was 0.2 $N$. (Efforts to use solutions which were 2 $N$ in metal, were unsatisfactory, because when such solutions contain considerable tin, crystals, presumably stannous fluoborate, separate). When using commercial hydrofluoric acid, containing 50 percent HF, and (an average of) 2 percent $H_2SO_4$, the following materials are required:

| | g./L. | oz./gal. |
|---|---|---|
| Basic lead carbonate | 142 | 19 |
| 50 percent hydrofluoric acid | 240 | 32 |
| Boric acid | 106 | 14 |
| Glue | 0.2 | 0.025 |

In the laboratory experiments commercial lead carbonate and boric acid, both of high purity, were used, but c. p. hydrofluoric

[8] Trans. Amer. Electrochem. Soc., 1919, *36*, 243.

acid was employed to avoid errors due to the presence of sulphuric acid in the commercial material. Glue was not added to the solutions unless specifically stated.

### *Tin Fluoborate.*

No satisfactory method was found for the commercial preparation of tin fluoborate solutions. Apparently there is no commercially available tin compound (such as the hydroxide) which can be dissolved in fluoboric acid, without introducing any other acid or metallic radicals. In the laboratory such solutions were prepared by electrolysis of fluoboric acid with a tin anode, and a platinum cathode enclosed in a porous cup. The process was inefficient however, as considerable tin entered the cup and was deposited upon the cathode.

### *Lead-tin Solutions.*

These solutions were obtained by electrolysis with tin anodes, of the lead solutions as above prepared, until the desired amount of tin, as determined by analysis, was present in the solution.

### *Analysis of Solutions.*

No difficulty was experienced in the gravimetric determination of lead by the usual precipitation with sulphuric acid and filtration upon a Gooch crucible. The tin in the solutions (if the latter were kept in contact with tin or lead-tin alloys) was found to be entirely in the stannous condition. The following method for its determination is rapid and gives results that are certainly accurate to one percent of the tin content.

A 0.2 *N* permanganate (6.3 g. $KMnO_4$/L.) solution is standardized in the usual way against sodium oxalate, and the tin value is calculated directly from the ratio $Na_2C_2O_4$:Sn. A 0.2 *N* ferric chloride solution is prepared by dissolving about 55 g./L. of $FeCl_3.6H_2O$, and adding about 5 cc./L. of concentrated hydrochloric acid (or slightly more if necessary to maintain a permanently clear solution). It is not necessary to standardize the ferric chloride solution. The method depends upon the addition to the lead-tin solution, of an excess of the ferric solution and the titration of the resultant ferrous salt with permanganate. As is well known, direct titration of the tin solution with perman-

ganate is not satisfactory. The use of ferric sulphate instead of chloride causes erratic results, possibly because the precipitated lead sulphate occludes some of the stannous salt.

A 10 cc. sample of the plating solution is diluted to 100 cc. and about 50 cc. of the ferric solution is added, or enough to produce a distinct yellow color. The solution is then titrated with permanganate until a pink coloration is produced which persists for at least one minute. The results should be corrected for the small amount of permanganate (usually about 0.2 cc.) required to produce the same pink color in 50 cc. of the ferric solution similarly diluted.

### *Acidity.*

Repeated attempts were made to determine by titration the free fluoboric acid, but without success, as the results were greatly influenced by dilution, time of standing after dilution, etc. Under strictly comparable conditions it may be possible to obtain results which will be of rough value in factory control but no great dependence can be placed on them. There is a great need for a thorough study of the constitution and behavior of the so-called "fluoboric acids." Fortunately in lead-tin deposition the metal content of the solutions remains nearly constant, so that aside from mechanical losses, there is not much possibility of a change in the acidity.

### *Stability of Solutions*

Occasionally it was found that upon standing for a week or more a cloudiness appeared and a white precipitate gradually formed in the lead-tin solutions. This precipitate upon analysis was found to contain tin, principally in the stannous condition, and to be almost free from lead and from fluorine. Apparently, therefore, it is some form of stannous hydroxide, containing at most a small amount of stannic hydroxide (or metastannic acid). The conditions leading to its formation could not readily be defined. In some cases when two portions of the same solution were preserved under apparently identical conditions it would appear in one within a short time, and not for some time if at all in the other. Increased acidity or increased metal concentration of the solutions retarded its formation but did not always prevent

it. In general it appeared more rapidly in solutions that were not in use than in those that were subjected to electrolysis. It is impossible to state from the evidence secured whether its formation was contingent upon (a) partial oxidation of the stannous salt, (b) precipitation of a colloid, (c) transformation from a stannous to a meta-stannous acid, or (d) a change in the equilibrium between the hydrofluoric and boric acids. From a purely practical standpoint the formation of this precipitate does not materially affect the operation of the plating solutions, but undoubtedly it does produce some changes in their composition and thereby renders their control more difficult. After the first few weeks of operation no further precipitation occurs.

### *Analysis of Anodes and Cathodes.*

Tin and lead were determined in the anodes by the usual gravimetric methods. (Where approximate results are sufficient, only tin may be determined, and the lead computed by difference). The same procedure was used in some cases for the analysis of the cathode deposits but in most cases their composition was computed by the following method.

In repeated tests, based on the weight and actual analysis of the cathode deposits, it was found that the cathode efficiency for tin plus lead was in every case (under the conditions employed) almost exactly one hundred percent. This being the case, it is possible to calculate the ratio of tin to lead in a deposit of given weight produced by a definite quantity of electricity. To determine the latter, a copper coulometer may be employed, or (as shown previously) a lead fluoborate bath may be used as a lead coulometer. In the latter case it suffices to know the actual (or relative) weights of (a) lead and (b) lead plus tin, deposited by the same current. A simple formula for this calculation may be derived as follows:

Let a = wt. of Pb
b = wt. of Pb +Sn
x =No. of faradays used to deposit tin
1 faraday = 103.6 g. (one chem. equiv.) of Pb
1 " = 59.35 g. (one chem. equiv.) of Sn

Therefore for each faraday used in depositing t i n, the deposit will weigh 103.6 — 59.35 = 44.25 g. less than that of the pure lead deposited by the same current.

$$a - b = 44.25\ x$$

or

$$x = \frac{a - b}{44.25}$$

$$59.35\ x = \frac{59.35\ (a - b)}{44.25} = \text{wt. Sn}$$

$$\frac{59.35\ (a - b)}{44.25} \times \frac{100}{b} = \text{percent Sn}$$

$$134.1\ \frac{a - b}{b} = \text{percent Sn in deposit}$$

*Example:*

If with the two baths in series, the deposit of lead weighs 200 g. and that of lead + tin weighs 146.4 g., then

$$\text{Percent Sn in deposit} = 134.1\ \frac{200 - 146.4}{146.4} = 49.1 \text{ percent.}$$

This method of calculation gave results which agreed with those by chemical analysis within one percent. Its use reduced very greatly the analytical work involved in this investigation. It can be applied approximately to large scale operation if the number of ampere hours can be measured fairly accurately and the weight of the deposit determined.

It is convenient in research work to compute the composition also in equivalent percentages of lead and tin, in order to permit convenient comparison between the composition of the deposits and the solutions.

## V: ELECTRODE POTENTIALS.

There is considerable uncertainty as to the values and even the relative order of the normal potentials of lead and tin, the most recent values (referred to the normal hydrogen electrode) being —0.12 V. for lead and —0.10 V. for tin.[9] Regardless of the exact

[9] Le Blanc, "Lehrbuch des Electrochemie," 7th Edition.

values, it is obvious that the potentials of the two metals lie so close to each other that even small changes in the metal ion concentrations of their respective solutions may change the relative order of the two metals. For present purposes, therefore, the actual values of the potentials are of much less significance than their relative values in the particular solutions concerned.

A few attempts were made to measure the relative potentials of tin and lead in fluoborate solutions containing tin or lead or both. It was found that when tin was immersed in a lead fluoborate solution it became coated with lead so rapidly that no true potential could be measured. Similarly when lead was immersed in a tin fluoborate solution tin was precipitated upon it. The conclusion from these measurements was that in fluoboric acid, the lead and tin have very nearly the same potential, and depending upon the respective metal ion concentrations, either may displace the other.

If then a lead solution is agitated with metallic tin, and a similar tin solution with metallic lead, until no further action occurs, solutions of the same final composition, in which the two metals must have the same potential, should be secured. (This is based upon the assumption that no appreciable chemical solution of either of the metals occurs, an assumption confirmed by the fact that the total metal content of the solutions remains practically constant.) The results obtained from a number of such experiments are shown in Table I.

From experiments 1a and b in Table I it is evident that in a fluoborate solution which is normal in total metal and 0.5 *N* in free acid, the same equilibrium is reached, whether tin displaces lead or vice versa. Experiments 2a and b show that this equilibrium is not affected by the presence of glue in the amounts normally used. For practical purposes we may, therefore, state that in such a solution an equilibrium is reached when there are four equivalents of tin to one of lead. This indicates that in these solutions, tin has a greater solution pressure than lead; in other words it has a more negative potential, or is higher in the series than lead; thus reversing the more recently adopted order.

Experiments 3a, b and c, show that this equilibrium is influenced appreciably by the acid concentration, and that the tin content at

equilibrium decreases with increasing acidity. Experiments 4a, b and c, show that increasing the total metal content also decreases the proportion of tin at equilibrium; and similarly from experiments 5a, b and c, it is seen that with very low metal concentration, the proportion of tin is greatly increased.

The principal significance of these "equilibrium ratios" for any composition of solution, is that during electrolysis of such a solution there must always be a tendency for this equilibrium to be reached. The practical significance of this fact will be referred to later.

TABLE I.

*Equilibria in Lead-Tin Solutions.*

| Expt. | Original Composition | | | | Metal added | Final Composition | | | $\frac{N\ Sn}{N\ Pb}$ |
|---|---|---|---|---|---|---|---|---|---|
| | Pb | Sn | Free $HBF_4$ | Glue g./L. | | Pb | Sn | Pb+Sn | |
| | *N* | *N* | *N* | | | *N* | *N* | *N* | |
| 1a | 1.00 | —— | 0.50 | —— | Sn | 0.19 | 0.82 | 1.01 | 4.3 |
| b | —— | 1.00 | 0.50 | —— | Pb | 0.19 | .81 | 1.00 | 4.2 |
| 2a | 1.00 | —— | 0.50 | 0.2 | Sn | 0.20 | .80 | 1.00 | 4.0 |
| b | —— | 1.00 | 0.50. | 0.2 | Pb | 0.19 | .82 | 1.01 | 4.3 |
| 3a | 1.00 | —— | —— | —— | Sn | 0.15 | .86 | 1.01 | 5.7 |
| b | 1.00 | —— | 0.10 | —— | Sn | 0.15 | .87 | 1.02 | 5.8 |
| c | 1.00 | —— | 0.50 | —— | Sn | 0.19 | .82 | 1.01 | 4.3 |
| 4a | 1.5 | —— | —— | —— | Sn | 0.23 | 1.25 | 1.48 | 5.4 |
| b | 1.5 | —— | 0.15 | —— | Sn | 0.26 | 1.25 | 1.51 | 4.8 |
| c | 1.5 | —— | 0.75 | —— | Sn | 0.36 | 1.16 | 1.52 | 3.2 |
| 5a | 0.20 | —— | —— | —— | Sn | 0.006 | 0.19 | 0.20 | 31.0 |
| b | 0.20 | —— | 0.02 | —— | Sn | 0.011 | 0.19 | 0.20 | 17.0 |
| c | 0.20 | —— | 0.10 | —— | Sn | 0.021 | 0.18 | 0.20 | 8.8 |

## VI: RELATION BETWEEN TIN-LEAD RATIO IN SOLUTIONS AND DEPOSITS.

As it has been found empirically that a solution such as was used in experiments 1 and 2 (Table I) operates satisfactorily and from Table I it is evident that in such a solution the equilibrium ratio is not markedly affected by moderate changes in concentration or acidity, this solution was used in the subsequent experiments. The purpose was to determine the relation between the metal ratios in the solution and in the deposit produced under

any given conditions. Necessarily the conditions such as volume of solution, degree of agitation, etc., were empirically selected, and hence the exact values may not be reproducible under other conditions. The shape of the curves secured (Fig. 1), is probably, however, of general significance.

In each of these experiments about 1300 cc. of lead fluoborate solution of the above composition (1.0 *N* Pb, 0.5 *N* free $HBF_4$) was electrolyzed with tin anodes and rolled steel cathodes with approximately equal areas (10 x 10 cm. or 4 x 4-in.). A lead bath with lead anodes was operated in series to serve as a coulometer, or in some cases a copper coulometer was used. The bath with tin anodes was agitated by a mechanical stirrer to insure uniformity in the composition of the solution and the deposit. (In a few experiments without agitation it was found that stratification of the solution occurred and the composition of the cathode deposit was not uniform).

At intervals of one hour the lead and lead-tin deposits were weighed, and the composition of the latter was computed as above described. A sample of the lead-tin solution was then taken and analyzed. Since the cathode composition as computed was the average for the period, it was plotted against the average composition of the solution for the same period. The results of such a series of experiments, conducted with a cathode current density of 0.8 amp./dm.$^2$ (7 amp./sq. ft.) are shown in Fig. 1, curve A. An almost identical curve was obtained by using lead anodes in a tin fluoborate solution; in fact the dotted portion of A is based on these latter measurements. From curve A it may be noted that the deposit consists of almost pure lead until a relatively large amount of tin is present in the solution, and that at a point corresponding to approximately 0.81 *N* tin and 0.19 *N* lead (and only at this point) the deposit has the same ratio of tin and lead as are present in the solution. It should be noted that this corresponds to the equilibrium solution. Curve D is the hypothetical curve for equal metal ratio in deposit and solution, a condition that could be reached only if at all points the two metals have the same potential.

If the current density is increased to 1.6 amp./dm.$^2$ (14 amp./sq. ft.) the curve B is obtained, differing from A only

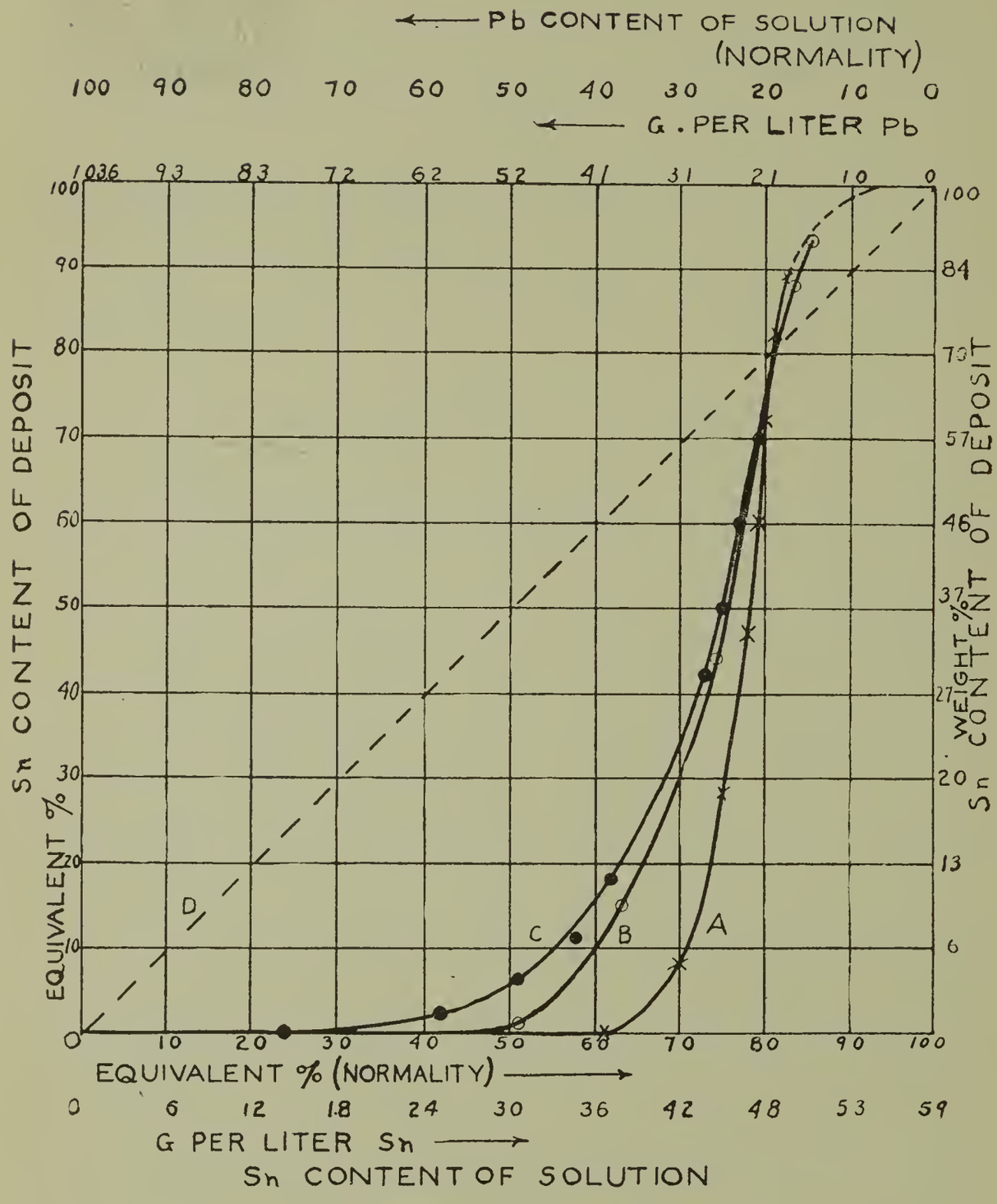

Pb CONTENT OF SOLUTION
(NORMALITY)
100 90 80 70 60 50 40 30 20 10 0
G. PER LITER Pb
103 96 93 83 72 62 52 41 31 21 10 0
Sn CONTENT OF DEPOSIT
EQUIVALENT %
Sn WEIGHT % CONTENT OF DEPOSIT
100 84 73 57 46 37 27 20 13 6
D
C
B
A
EQUIVALENT % (NORMALITY)
0 6 12 18 24 30 36 42 48 53 59
G PER LITER Sn
Sn CONTENT OF SOLUTION

Fig. 1.

RELATIVE COMPOSITION OF LEAD-TIN SOLUTIONS AND DEPOSITS

A. 0.8 amp/dm$^2$ (7 amp/sq.ft.)
B. 1.6 amp/dm$^2$ (14 amp/sq.ft.)
C. 0.8 amp/dm$^2$ (7 amp/sq.ft.) in presence of glue.
D. Hypothetical curve for equal metal ratio in solution and deposit.

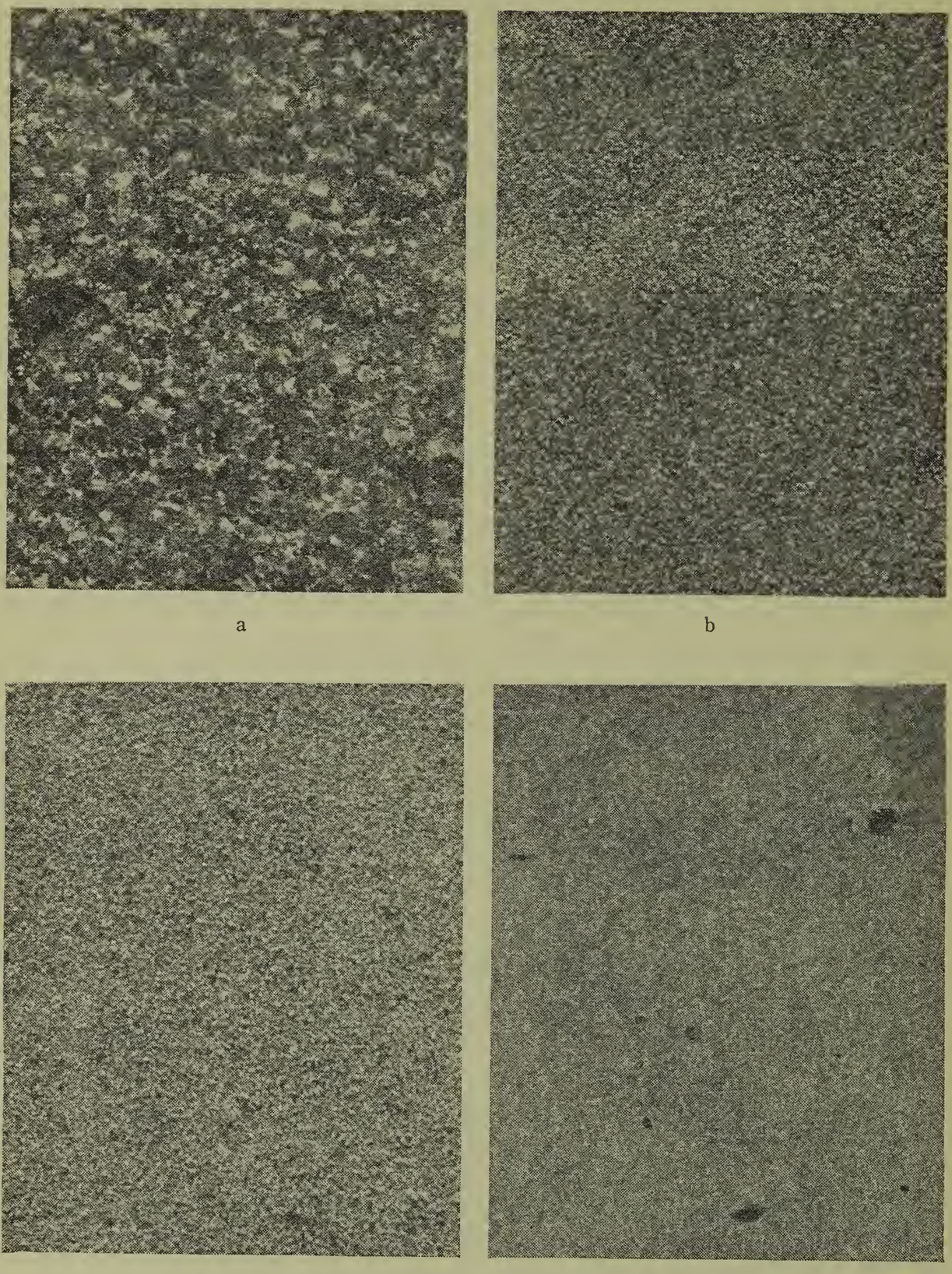
in that the deposit contains relatively more tin, with the solutions of lower tin content, *i.e.*, it approaches curve D. This is equivalent to stating that in these solutions tin is thrown out more readily the higher the current density, another evidence that the tin has a greater solution pressure than the lead. With increasing tin content the curves are almost identical and, as previously, at the point of equal potential, the deposit has the same metal ratio as the solution.

Curve C, based on deposits produced at 0.8 amp./dm.$^2$ (7 amp./sq. ft.) in solutions containing glue, is of much interest as it indicates that the effect of the glue is equivalent to an increase in current density. Such an effect can be readily explained if we accept the theory proposed by V. Engelhardt,[10] according to which the influence of such colloidal addition agents as glue is due to the formation at the points of momentarily highest current density, of a "wandering diaphragm" which reduces the current density at those points or may insulate them. If such is the case, it is obvious that the true effective current density of deposition is higher than that computed from the current and the total cathode area, as those parts of the surface not so insulated must have a higher current density than the average. If then the metal is actually deposited at a relatively higher current density, it should have a higher tin content. It is interesting to note that the decrease in crystal size usually produced by the presence of colloids, is similar to that obtained by increasing the current density. Further experiments in this connection will be of interest.

## VII: RELATION BETWEEN THE COMPOSITION OF THE ANODE AND THE CATHODE.

If, as above shown, the composition of the deposit produced at a given current density is determined by the composition of the solution, it is difficult to see how the composition of the anode per se has any effect. Actual experiments showed that if a solution of given composition was electrolyzed for a short period, the deposit had exactly the same composition, regardless of whether the anode was of platinum, lead, tin, or a lead-tin

[10] Trans. Amer. Electrochem. Soc., 1912, **21**, 332.



a b

c d

FIG. 2

Structure of Lead-Tin Deposits (x 35). From Fluoborate Solutions. All Deposits are 0.025 mm. (0.001 in.) thick, produced at 0.8 amp./ dm.$^2$ (7 amp./sq. ft.).

a—Tin

b—Lead

c—50 equiv. percent each of tin and lead

d—As in c—but from solutions containing glue

alloy. In other words the anode can affect the deposit only insofar as it produces changes in the composition of the solution. Otherwise we would have to assume "action at a distance", such as has not thus far been observed.

It is obvious, however, that a lead-tin solution can continue to produce a deposit of uniform composition only if the two metals are replenished at the same rate as they are deposited, which can in general be accomplished only if the anodes have the same composition as the cathode deposits, and if the anodes dissolve completely. At the point of equilibrium potential (0.81 *N* Sn and 0.19 *N* Pb) the deposits have the same metal ratio as in the solution, and therefore such a solution may be operated uniformly with corresponding anodes. If, as is usually the case, it is desired to obtain deposits of lower tin content than the above (which corresponds to 71 wt. percent of tin), it is important to determine the effect of operating with anodes of other compositions. If the equilibrium solution is operated with anodes containing 50 wt. percent of tin (63 equivalent percent), the tin content of the deposit will decrease but will remain slightly above that of the anodes even after long operation. Similarly if anodes with 75 wt. percent of tin (84 equivalent percent) are used in the equilibrium solution, the deposits will, even after long operation, contain less tin than the anodes. In other words the solution and therefore the deposit will always tend toward the equilibrium value. This adjustment is brought about by the fact that in the solutions containing more tin than corresponds to the equilibrium, the lead has a greater solution pressure than the tin, and hence dissolves more readily from the anode than does the tin, and a sludge high in tin is produced. Exactly the reverse occurs if the tin content of the solutions is below the equilibrium value.

Let us assume that it is desired to produce a deposit containing 50 wt. percent (63 equivalent percent) of tin. If 50-50 lead-tin anodes are used in a solution of the above metal content and acidity, (1.0 *N* in metal and 0.5 *N* free $HBF_4$), regardless of the original metal ratio in the solution, a deposit will finally be produced which contains more than 50 wt. percent of tin, *e. g.*, 55

percent; and the sludge will be found to consist almost entirely of lead. For continuous operation, therefore, the anodes should have less than 50 wt. percent of tin, *e. g.,* about 45 percent. The exact composition required will depend upon the volume of solution, relative anode and cathode areas, etc. Within the range from 25 to 75 wt. percent of tin, it is possible to produce continuously deposits which, subject to the above limitations, will have a composition which remains constant within a few percent. Below this range it is not feasible to operate, as in the solutions required to produce such deposits, the potentials of lead and tin are sufficiently different that the corresponding anodes corrode very irregularly and consequently change the composition of the solution. Moreover, in this region even slight changes in the current density produce a marked effect upon the composition of the deposits.

## VIII: STRUCTURE OF THE DEPOSITS.

Direct observation of the deposits shows that those containing lead and tin have a decidedly finer structure than those of lead or tin produced under corresponding conditions. It appears, therefore, that the lead and tin each acts as an "addition agent" upon the other. Such an effect of one metal upon the structure of another is not dissimilar to that recently observed by one of the authors[11] in macroscopic layers of two metals alternately deposited. It is significant that in a series of deposits ranging from pure lead to pure tin, the finest grained were those containing equivalent (not equal) amounts of the two metals, *i.e.,* about 37 percent by weight of tin. The relative size of the crystals is illustrated in Fig. 2, a, b and c. The glue caused the lead-tin deposits to be still finer grained, as shown in Fig. 2d.[12]

As previously stated, attempts to study the internal crystal structure of these deposits were unsuccessful. The results obtained simply indicated that the two metals are very intimately mixed, with no evidence of orientation.

[11] W. Blum, "Structure of Alternately Deposited Metals," Trans. Amer. Electrochem. Soc., 1921, 40, 307.

[12] The authors are indebted to Mr. H. S. Rawdon of this Bureau for the preparation of these photographs.

## IX: CONCLUSIONS.

1. Lead and tin have nearly equal potentials in fluoborate solutions, but under similar conditions the tin appears to have the lower potential, *i.e.*, the greater solution pressure.

2. Lead or tin may each displace the other from fluoborate solutions, depending upon their respective metal ion concentrations.

3. Solutions which are 1.0 *N* in metal and 0.5 *N* in free $HBF_4$, when agitated with tin or lead, reach equilibrium at about 0.81 *N* Sn and 0.19 *N* Pb, because then the two metals have the same potential. This equilibrium is not affected by glue, but is influenced appreciably by the acidity and total metal concentration.

4. The cathode efficiencies under normal conditions are so nearly 100 percent that the composition of the deposits can be calculated from the weight of metal deposited by a given quantity of electricity. The latter may be measured with a lead or copper coulometer.

5. The composition of the deposits obtained under otherwise similar conditions, depends upon the metal ratio in the solution. The ratio of the metals in the deposit is the same as that in the solution, only when the solution has the equilibrium composition as above defined.

6. Increasing the current density, in solutions of low tin content, increases the tin content of the deposit.

7. The presence of glue has the same effect upon the metal ratio in the deposit, as has an increase in current density.

8. The composition of the deposit is not influenced by that of the anodes, except as these cause changes in the solution.

9. Continuous operation with anodes containing more or less tin than corresponds to the equilibrium solution (81 equivalent percent or 71 wt. percent of tin) causes the formation of deposits differing from the anodes always in the direction of this equilibrium. Thus if the anodes contain less than 71 wt. percent of tin, the deposits will contain more tin than the anodes, and *vice versa*.

10. To produce deposits containing about 50 wt. percent of tin, the solution may be prepared by electrolyzing a lead fluoborate

solution (as previously described) with tin anodes, until, as determined by calculation or analysis, the deposit contains nearly the desired tin content. During this operation the solution should be agitated or at least frequently mixed. Lead-tin anodes are then used which contain somewhat less tin than is desired in the deposits. A current density of 0.5 to 1.5 amp./dm.$^2$ (4.7 to 14 amp./sq. ft.) may be employed.

11. Deposits of lead and tin have a finer crystalline structure than lead or tin deposited under similar conditions.

12. In the presence of glue the deposits are still finer grained.

There has not been thus far an opportunity to make detailed studies of the conditions employed in the commercial process. The above conclusions, based on laboratory experiemnts, are confirmed, however, by the observations of the plant operation thus far made.

The authors desire to express their thanks for the assistance of C. T. Thomas and J. H. Winkler of this Bureau in conducting these experiments, and for suggestions from James S. Groff of the Naval Torpedo Station at Newport, R. I.

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## DISCUSSION.

C. H. Proctor[1]: I want to explain where a solution of this type can fit in nicely. In my travels several years ago one of the members of the Electro-Platers' Society connected with the Kellogg Switchboard Company, Chicago, had a proposition put before him. It is difficult to soft-solder steel direct, and so we copper-plated the articles, but as it was not a satisfactory method, they reverted to hot tin coatings. You can imagine that with small parts, which laid close together, it was difficult to tin them satisfactorily. There was quite considerable waste of tin, and the matter was put up to Mr. Bedord, the plater, to see if it was possible to deposit a coating of tin and lead.

I happened to be well acquainted with Mr. Bedord, and we discussed the proposition. Finally it was decided to use a solu-

[1] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.

tion of potassium hydroxide and tin chloride. Then the difficulty was how to get lead into solution, so it was decided to use litharge, and hang the material in bags in the tin solution. The method worked out successfully, and they are using it today for plating thousands of steel parts with the coating of tin and lead by using a hot solution.

They had some difficulty in arranging the bath for this particular purpose, as the high caustic solutions are very destructive. We arranged the ordinary type of large vitreous baskets so that they could be set in the plating tank in the hot solution. Conducting wires were carried from the bottom of the baskets by the proper methods, and the results were satisfactory. We realize that a fluo-lead and tin solution possibly would have greater depositing power than the sodium hydroxide solution, but still the latter fits nicely, and I think it can be used to a beneficial extent in many plants where they have to do considerable soldering on small parts that rust readily.

I might also further state, in connection with Dr. Blum's paper, that if any one is interested in getting the tin fluoride solution they can take sodium stannate and dissolve it in hydrofluoric acid. I have made some experiments lately with straight sodium stannate solutions, using 8 to 16 oz. per gallon (60 to 120 g. per L.) and find it an efficient solution. Just the deposit of tin alone will be satisfactory as a base for soldering operations upon steel.

C. J. WERNLUND[2]: May I inquire whether greater thicknesses of deposit could be made successfully?

WM. BLUM: We have made deposits up to 0.01 inch (0.3 mm.) or more; I think in the actual work they are doing at the torpedo station, they are depositing from 0.003 to 0.005 inch (0.076 mm. to 0.13 mm.).

J. W. RICHARDS[3]: I want to call attention to the fact that Dr. Blum's method of calculating the composition from the weight of deposit, instead of making an analysis, only applies where the chemical equivalents are wide apart. Where they are close together as with copper and zinc, you cannot use any such method.

[2] Research Laboratory, Roessler & Hasslacher Chemical Co., Perth Amboy, N. J.
[3] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

I was much interested in Dr. Blum's statement that the composition of the deposit on the cathode was independent of that of the anode; it is so much in line with what I have always taught in electrolysis, that the cathode does not know what is going on at the anode. I think that is a fruitful statement of electrochemical theory.

WM. BLUM (*Communicated*): Through an oversight, no mention was made in our paper of the careful study of the relative potentials of lead and tin in perchlorate solutions, conducted by A. A. Noyes and K. Joabe.[4] These authors also allowed the metals to come into equilibrium in the solutions, a procedure previously employed by O. Sackur. At equilibrium they found the ratio of tin to lead was 2.98, as compared with 4.2 in our admittedly approximate measurements. According to their observations, however, which we have confirmed over an even wider range, the ratio varies with the metal concentration and acidity.

[4] Journ. Am. Chem. Soc., 1917, **39**, 1537.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, October 1, 1921, President Acheson Smith in the Chair.*

# THE STRUCTURE AND PROPERTIES OF ALTERNATELY ELECTRODEPOSITED METALS.[1]

By William Blum[2].

## Abstract.

If relatively thin layers of nickel are interposed during the deposition of copper, the deposit has a much higher tensile strength than has pure copper deposited under similar conditions. It is shown that this effect is due to the influence of the nickel layers in restraining the growth of the copper crystals. The same effect is observed with layers of copper and silver, or even with layers of copper from the sulphate and cyanide solutions respectively. The principle has been applied in the electrolytic reproduction of engraved plates.

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## I: Introduction.

A few years ago attempts were made by the U. S. Bureau of Engraving and Printing to reproduce their printing plates by electrodeposition. It was then found that plates 0.25-inch thick, consisting entirely of electrodeposited copper (with a nickel printing face) did not possess sufficient strength, *i. e.*, they bent when in service upon the presses. Mr. Geo. U. Rose, Jr., chief of the Engraving Division, who was conducting these experiments, conceived the idea of "re-enforcing" the copper plates by the deposition of layers of nickel at intervals through the copper. He then found that plates so produced possessed the necessary strength to meet their requirements. This process of depositing alternate layers of nickel and copper, which has been patented by Mr. Rose,

[1] Manuscript received August 20, 1921. Published by permission of the Director of the Bureau of Standards.

[2] Chemist, Bureau of Standards, Washington, D. C.

is employed in the new electrolytic plant of the Bureau of Engraving and Printing, which was designed and installed under the supervision of the Bureau of Standards.[3]

## II: PRINCIPLES INVOLVED.

The purpose of this paper is to show that in so apparently trivial an innovation as the alternate deposition of two metals, a new principle possibly of wide application, is involved. Consideration by the author of the effect of the layers of nickel led to the thought that this is probably due not so much to the higher tensile strength of the nickel as to the influence of the nickel layers upon the structure and properties of the intervening copper. A few simple experiments and photographs showed that such is the case. In brief, it was found that each layer of nickel prevents the further growth of the copper crystals, and thereby influences the physical properties of the copper.

It has long been recognized that in the deposition of a metal the initial deposit is usually fine grained, but that the crystals become larger as the deposit increases in thickness. This was well illustrated in the photographs showing the structure of electrotyping copper.[4] If, as may generally be assumed, fine grained deposits have the greatest hardness and tensile strength, conditions leading to the formation of fine crystals are usually desirable, especially high current density, low temperature and agitation. For the thickness used in regular electrotyping, *i. e.*, up to 0.25 mm. (0.010 inch) there is no difficulty in securing relatively hard copper deposits by the application of these principles. When, however, as in the case in question, a thickness of 6 mm. (0.25 inch) or more is required, the use of a high current density leads to the excessive formation of "trees." Moreover, with large plates the degree of agitation is practically confined to that obtainable by compressed air, and usually it is not feasible to apply artificial cooling to the solutions. In consequence most of the thick copper plates produced electrolytically in various plants have been deposited at low current densities and have had relatively low hardness and tensile strength.

[3] For a brief description of the process, cf. W. Blum and T. F. Slattery, Chem. and Met. Eng., 25, Aug. 24, 1921.

[4] W. Blum, H. D. Holler, and H. S. Rawdon. Trans. Amer. Electrochem. Soc. 1916, 30, 159.

## III: EXPERIMENTS.

If the effect of each layer of nickel is due to its influence in preventing further growth of the copper crystals, the actual change in mechanical properties, *e. g.*, tensile strength, should be determined not so much by the relative thickness of the nickel and copper layers, as by the frequency with which the nickel layers are interdeposited. In order to determine whether such is the case, a number of plates were prepared in which both the frequency and the thickness of the nickel layers were varied. For purposes of comparison a number of plates of pure copper were deposited. The plates were machined and ground to a smooth surface, after which specimens were cut and tested for tensile strength and elongation.[5] The results of the tests are shown in Table I.

On all these specimens an initial coat of nickel (about 0.025 mm. or 0.001 inch) was deposited. All the nickel layers were produced without agitation at a current density of 2 amp./dm.$^2$ (19 amp./sq. ft.) in "Watts' solution" containing

| | g./L. | oz./gal. |
|---|---|---|
| $NiSO_4.7H_2O$ | 240 | 32 |
| $NiCl_2.6H_2O$ | 15 | 2 |
| $H_3BO_3$ | 30 | 4 |

(from which as determined in subsequent experiments, relatively soft nickel is secured). The copper deposits were made in an agitated solution containing:

| | g./L. | oz./gal. |
|---|---|---|
| $CuSO_4.5H_2O$ | 200 | 27 |
| $H_2SO_4$ | 100 | 13 |

From the data in Table I it is evident that of those deposits which contained copper and nickel in the ratio of 10 to 1 (by thickness) by far the greatest strength was produced when the nickel layers were introduced most frequently. On the other hand the presence of twice the above proportion of nickel produced only a slightly increased strength. It is interesting to note the beneficial effect of increasing current density upon the strength and structure of the pure copper deposits, as has been pointed out by Bancroft[6] and recently illustrated by

[5] The author is indebted to Dr. L. B. Tuckerman of this Bureau, who kindly conducted these mechanical tests.

[6] Trans. Amer. Electrochem. Soc 1904, 6, 27.

TABLE I.

*Mechanical Properties of Electrolytic Copper and Copper-Nickel Plates.*

| Plate No. | Copper | | | | Nickel | | Thickness Ratio | Ultimate Tensile Strength | | Percent Above No. 2 | Elongation Percent (in 5 cm. or 2 in.) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Current Density | | Thickness of each layer | | Thickness of each layer | | | | | | |
| | amp./dm² | amp./sq. ft. | mm. | in. | mm. | in. | | Kg/cm² | lb./sq. in. | | |
| 1 | 3 | 28 | .... | .... | .... | .... | .... | 870 | 12300 | .. | 1 |
| 2 | 6 | 56 | .... | .... | .... | .... | .... | 1690 | 23990 | .. | 10 |
| 3 | 9 | 84 | .... | .... | .... | .... | .... | 1870 | 26600 | 11 | 10 |
| 4 | 6 | 56 | 0.25 | 0.01 | 0.025 | 0.001 | 10:1 | 2240 | 31900 | 33 | 8 |
| 5 | 6 | 56 | 0.125 | 0.015 | 0.0125 | 0.0005 | 10:1 | 2480 | 35300 | 47 | 9 |
| 6 | 6 | 56 | 0.063 | 0.0025 | 0.0063 | 0.00025 | 10:1 | 2890 | 41100 | 71 | 13 |
| 7 | 6 | 56 | 0.125 | 0.005 | 0.025 | 0.001 | 5:1 | 3010 | 42900 | 79 | 7 |

A B C

FIG. 1

Structure of Heavy Copper Deposits (x 100) Effect of Current Density

| Current Density | Ultimate Tensile Strength |
|---|---|
| a—30 amp./sq. ft. | 12,300 lb./sq. in. |
| b—60 amp./sq. ft. | 24,000 lb./sq. in. |
| c—90 amp./sq. ft. | 26,600 lb./sq. in. |

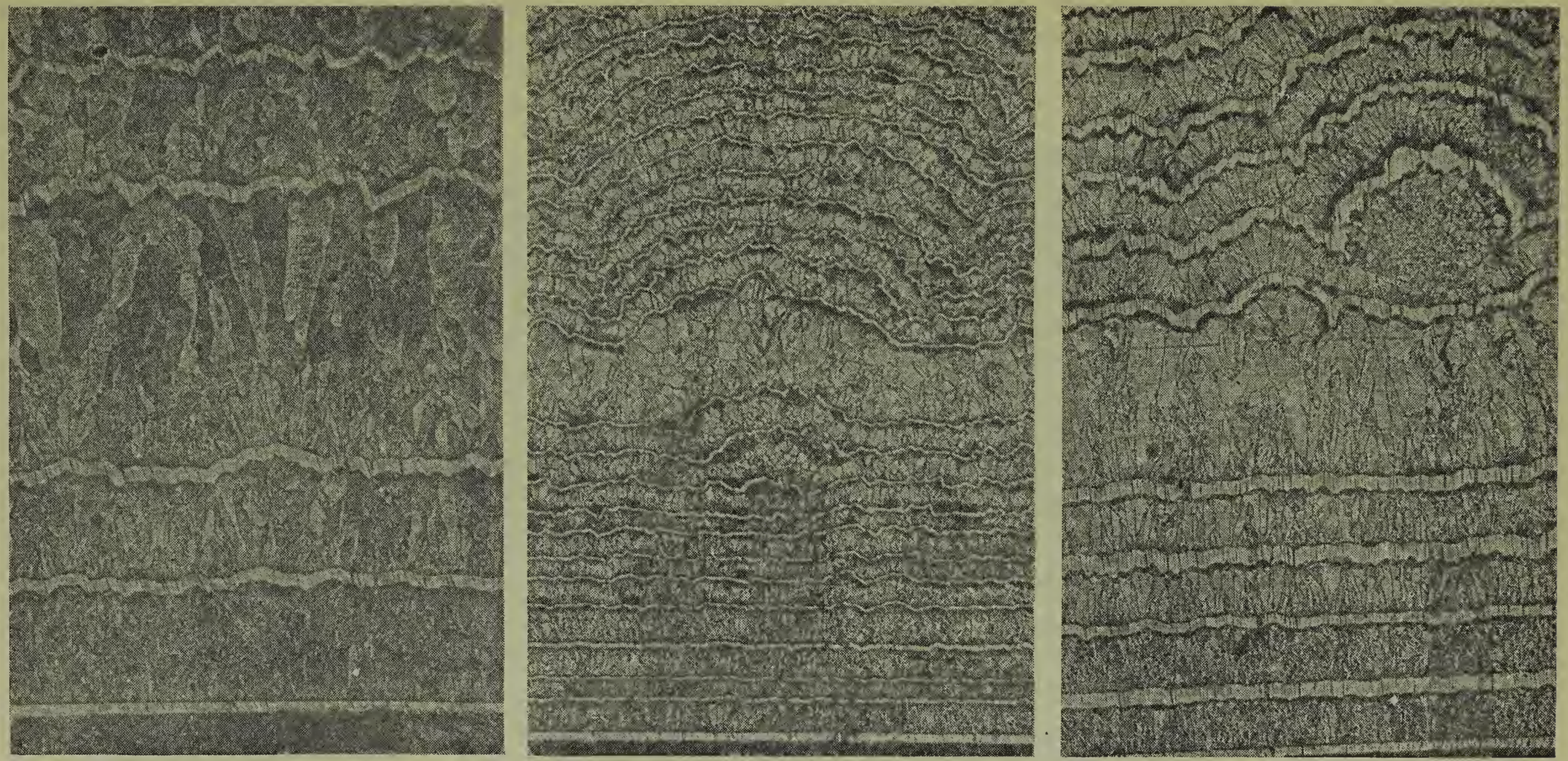
the author.[7] Thus in Fig. 1, it may be observed that as the current density is increased, the long crystals in A become broken up appreciably at the higher current density used in B; which finally leads to the formation of twinned crystals at still higher current densities. However, even at 6 amp./dm.$^2$ (56 amp./sq. ft.) marked treeing occurred, which was still more pronounced at higher current densities.

That the changes in strength produced by the nickel layers were caused principally by a decrease in the average size of the copper crystals, is illustrated by the photographs of Fig. 2. In each case it may be observed that the copper crystals increase in size as deposition continues, but that when a layer of nickel is interposed, further growth ceases, and new fine crystals are deposited. Also it is obvious that in Fig. 2, B, in which the nickel layers are most frequent, the average size of the copper crystals is smaller than in A or C. It is true, however, that the copper crystals become slightly coarser in each layer as the deposition continues, which explains why the nickel layers do not entirely eliminate the roughness of the deposits. No attempt was made in these experiments to determine the extreme effects which might be produced by very frequent alternation as, e.g., in a mechanically operated continuous process.

In addition to increasing the strength of the deposits, the presence of the nickel layers reduces materially the tendency to treeing. This is to be expected, as in effect a "tree" is simply a large crystal or series of crystals caused by favorable conditions. Among these is the high potential drop through the solution, which, under otherwise similar conditions, must accompany a high current density. Any procedure which will decrease the formation of trees is very helpful in permitting the use of higher current densities in the production of thick deposits. Waste of current and metal are thereby reduced, and the time and labor required for finishing are diminished.

That the above effects of alternation are not confined to these two metals is shown by Fig. 3, in which layers of silver (from the usual cyanide solution) are alternated with layers of copper from the sulphate solution. The choice of the two metals is

[7] Trans. Amer. Electrochem. Soc., 1919, 36, 57.



A B C

FIG. 2

Structure of Alternate Deposits of Copper and Nickel (x 100)

| Thickness Ratio Cu:Ni | Layers of each per inch | Ultimate Tensile Strength |
|---|---|---|
| a—10:1 | 90 | 32,000 lb./sq. in. |
| b—10:1 | 360 | 41,000 lb./sq. in. |
| c —5:1 | 170 | 42,000 lb./sq. in. |

limited only by the condition that, in the solutions employed, neither must cause deposition of the other by immersion to such an extent as to prevent proper adhesion of successive layers. (Where there is only a slight tendency for such deposition, it can be prevented by having the cathode connected in the circuit before introducing it into the solution).

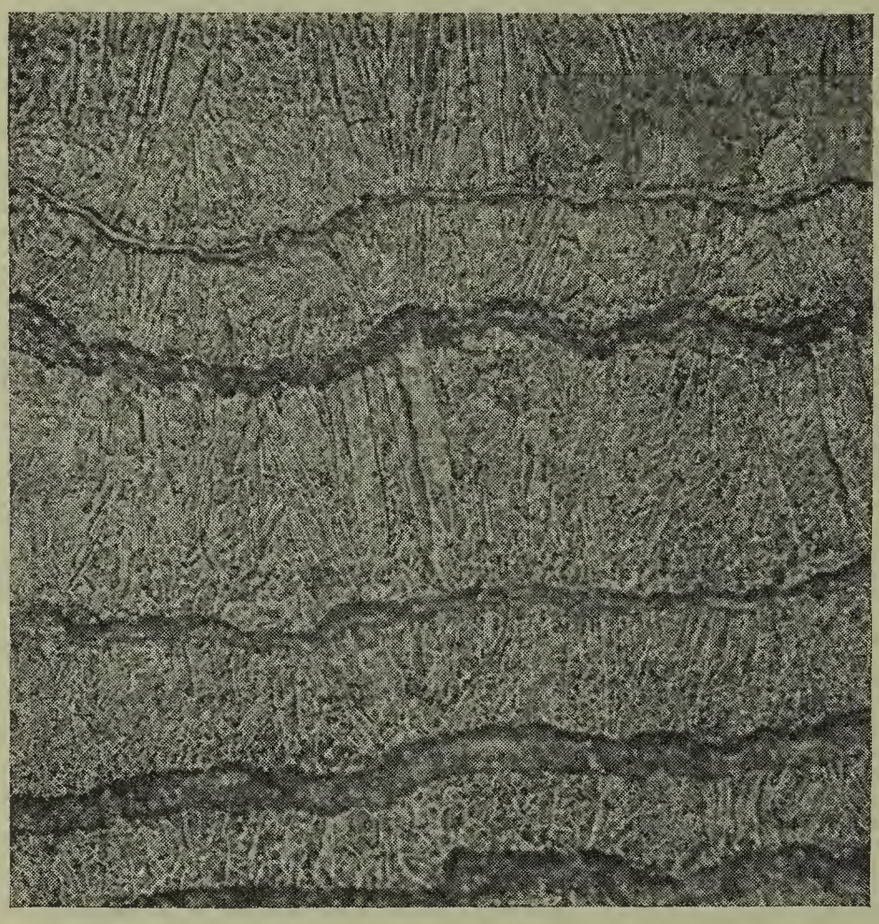


FIG. 3
Structure of Alternate Deposits of Copper and Silver (x 500)

If the process depends upon the different structure of the interdeposited metal, the same result should be accomplished if both layers are composed of the same metal, provided they have different crystalline structures. It is well known that copper deposited from a cyanide solution is much finer grained than that from sulphate solutions. Accordingly in one experiment layers of copper from a cyanide solution were interdeposited between the layers from the sulphate solution. As seen in Fig. 4, the structure of the "sulphate copper" deposits is affected in

just the same way, but not to so marked a degree, by the layers of "cyanide copper" as by nickel. No tensile strength tests were made on this deposit, but there is no reason to doubt that the change in structure was accompanied by an increase in strength.

## IV: APPLICATIONS.

The possible applications of this process may extend to many operations in which the presence of another metal, or of layers of the same metal is not objectionable. Copper is especially adapted to galvanoplastic operations, such as electrotyping, the

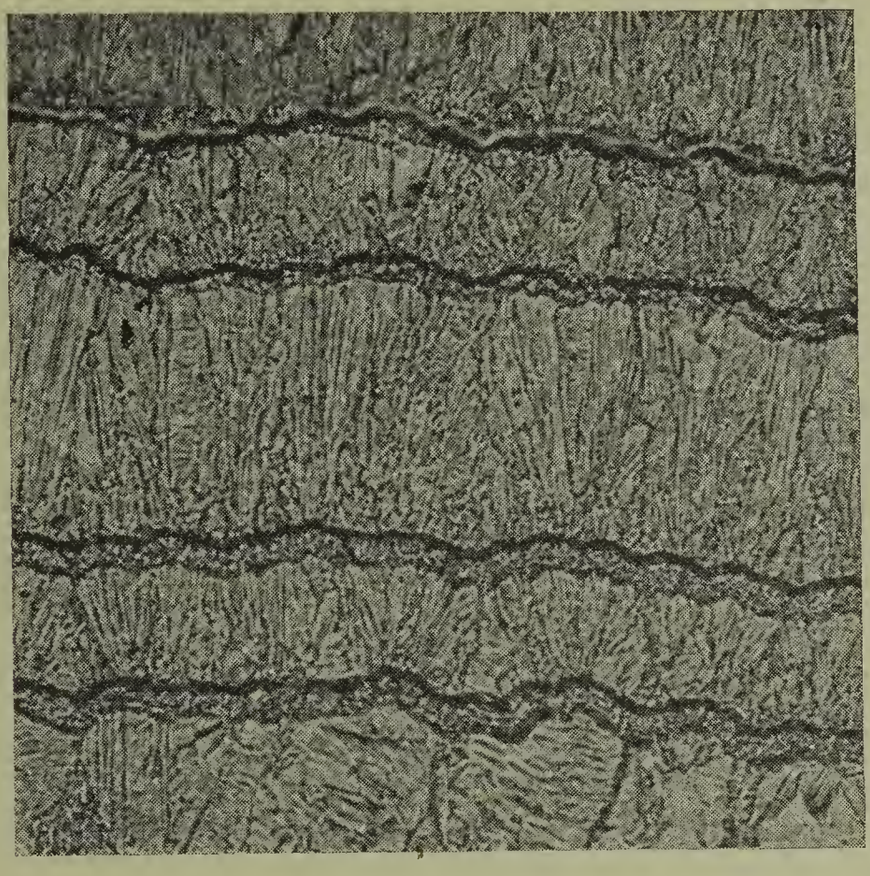


FIG. 4
Structure of Alternate Deposits of Copper from Sulphate and Cyanide Solutions (x 500)

reproduction of engraved plates, the manufacture of phonograph record matrices, and of tubes and other irregularly shaped articles. In all of these processes the introduction of nickel layers may be found advantageous, in producing greater strength, and permitting the use of higher current densities, and possibly of thinner deposits.

Of even greater interest than the immediate industrial applications of this principle, is its possible bearing upon other problems in electrodeposition. If macroscopic layers of one metal produce such a decided effect upon the structure of the layers of another metal, it is entirely reasonable to expect that if the layers were much thinner, and ultimately molecular, still more marked effects would be produced. In other words we would expect an electrodeposited alloy to have a much finer crystalline structure than either of its constituents deposited under similar conditions. This has been recently found by the author and his associates to be the case with lead-tin alloys.[8]

Similarly it is known that even small amounts of foreign metals in deposited metals, arising either from accidental impurities or from intentional additions to the bath, may exert profound effects upon the structure of electrodeposits. It appears reasonable to assume that at least part of their effect is due to hindering the normal crystal growth in the above described manner. Even the effects of those organic addition agents, which are known to be included in at least small amounts in the deposits, may be due largely to their mechanical retardation of the crystal growth. Viewed from this standpoint, the above observations are at least in general accord with the theory of the "wandering diaphragm moving boundaries" as proposed by Engelhardt[9] according to which the effect of colloids is caused by their migration to the cathode, accumulation upon points of (momentarily) highest current density, and consequent retardation of crystal growth at those points. The whole question presents a fascinating subject for investigation, and emphasizes the importance of a more extended study of the internal structure of electrodeposits.

The author is indebted to his associates, especially W. E. Bailey, H. E. Haring and L. D. Hammond, for assistance in the preparation and study of the plates described in this paper, and to H. S. Rawdon for the preparation of the photographs.

[8] W. Blum and H. E. Haring, "The Electrodeposition of Lead-Tin Alloys"—Trans. Amer. Electrochem. Soc., 1921, **40**, 287.

[9] Trans. Amer. Electrochem. Soc. 1912, **21**, 332.

## DISCUSSION.

LAWRENCE ADDICKS[1] (*Communicated*): Dr. Blum has presented some convincing photographs to support the argument that crystal growth in electrolytic deposits may be controlled by the deposition of thin layers of metal of different characteristics. The chief practical disadvantage in the use of two different metals is the metallurgical problem introduced in the working up of the scrap. For instance, the nickel layers in the electrotype plates would considerably decrease the value of the copper scrap produced.

A high current density appears to make a fine grain deposit, much in the same way as a rapid cooling of an aqueous solution of a salt will result in a fine crystallization. Practical objections are offered in the paper to the use of high current density.

The breaking down of large crystals into smaller ones may greatly improve the character of the copper, as is shown in the production of wire from wire bars, where the tensile strength is easily tripled. In this connection I am led to inquire whether it would be practicable to burnish the deposit more or less continually while it was being produced, having in mind the remarkably strong copper tubing produced by burnishing an electrolytic deposit in the process, more or less used abroad for producing high pressure steam piping. Such procedure would seem to be cheaper than plating with two solutions.

WM. BLUM: After this paper was submitted, I found an article by G. Grube and V. Ruse, in Zeit. f. Elektroch., 1921, **27,** 45, in which they showed by fine photographs that when deposits of copper are made from solutions containing large amounts of gelatin or glue, the copper and gelatin are in alternate layers. This is of present interest, even though their explanation of the formation of the alternate layers is not based upon the actual deposition of a layer of copper and then a layer of glue.

As stated by Mr. Addicks, the general disposal of copper-nickel scrap may be difficult. We hope to be able to use this scrap metal in making five-cent pieces. As to burnishing, I think, it would

[1] Consulting Engineer, New York City.

be more expensive to burnish a surface at intervals, which would involve a subsequent cleaning of that surface than simply to take the plates from one bath to another.

COLIN G. FINK[2]: I understood that the burnishing is done at present.

WM. BLUM: That is in the Elmore process, where it is burnished during the deposition; on a flat plate that seems hardly feasible.

G. B. HOGABOOM[3]: This paper opens up an entirely new field and the process described will prove of value for building up thick electrodeposits. As a matter of coincidence, Dr. Blum, without realizing it, answered one of the problems of the electroplaters which were presented before this Society[4].

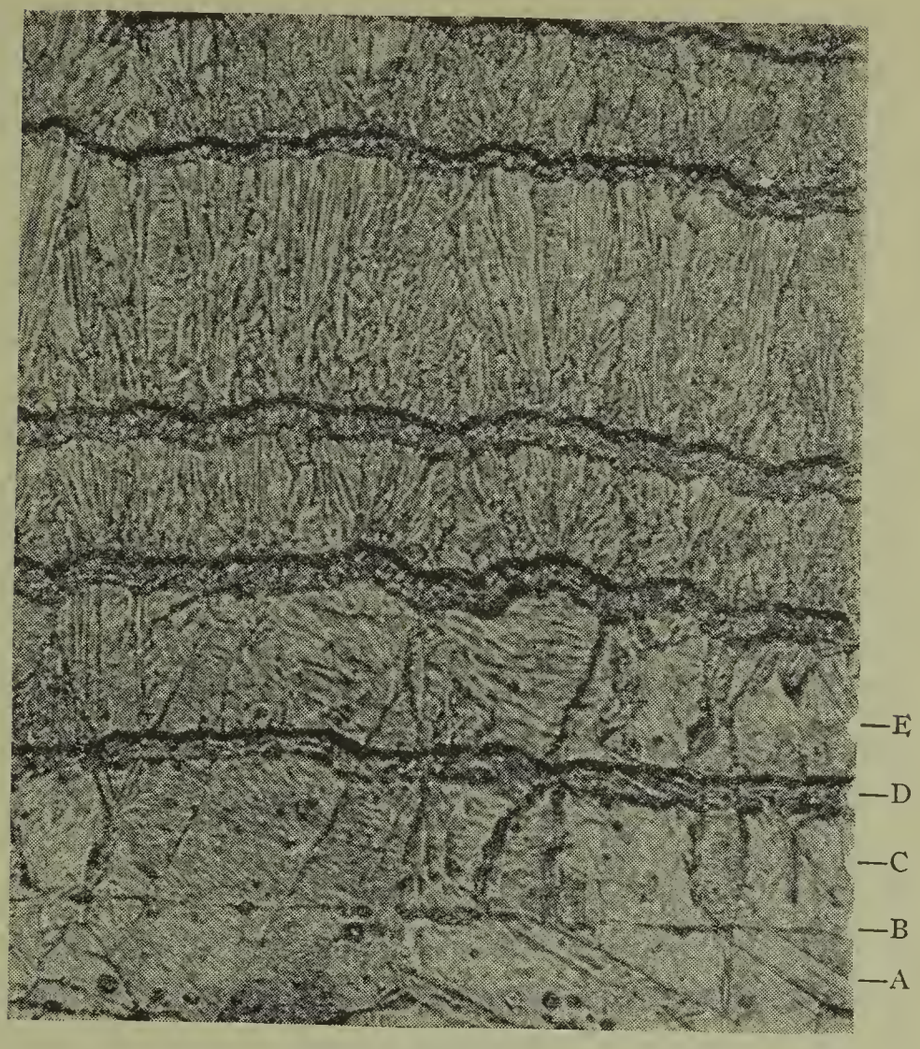
In the cyanide copper-acid copper deposits the structure of the base metal, which happened to be a piece of over-annealed copper, is clearly followed in the subsequent deposit for three alternate layers. Another view of Fig. 4 is given below in which this can be seen. It is believed that this is generally true, and that the structure of electrodeposits are coarse or fine, depending upon the structure of the base metal. Just what influence a colloid in the electrolyte would have is not known, but it is quite probable that a number of the results obtained by using the so-called addition agents can be questioned unless the structure of the metal used is uniform in all cases.

It would be interesting to know how the structure and composition of cast iron would influence the character of an electrodeposit of a metal; *e. g.*, copper. It is predicted that in deposits, such as commonly produced in electroplating, that the current, following the path of least resistance, will deposit the metal around spots of graphitic carbon or pearlitic structure, and gradually bridge over them. That may be the explanation of the porosity of thin electrodeposits. It also may be one of the factors in the trouble experienced by electroplaters in humid weather, known as "spotting out." If the deposit was porous and some moisture con-

[2] Consulting Electrometallurgist, New York City.

[3] Research Electroplater, Scovill Mfg. Co., Waterbury, Conn.

[4] Unsolved Problems of the Electro-Plater. By G. B. Hogaboom, Trans. Am. Electrochem. Soc. 1916, 29, 369.




Another View of FIG. 4.

A = Base metal-copper.
B and D = Copper deposit from cyanide solution.
C and E = Copper deposit from acid solution.

densed in one of the minute holes, an electrolytic action might be set up between the metal of the deposit and that of the article plated and cause a stain, which would be termed "spotting out."

C. H. PROCTOR[5]: That refers to the non-ferrous metals as well as the ferrous.

G. B. HOGABOOM: It is believed that "spotting out" of brass or bronze casting can be traced to the lack of deposit or the bridging over of minute gas pockets or oxide inclusions. The latter may become wet with the electrolyte, and then be bridged over by the deposit. In this case a minute blister would be formed, under which there would be a small drop of the electrolyte. Upon standing there would be an electrolytic action, and the solution gradu-

[5] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.

ally find its way through the deposit and cause a case of "spotting out." Note the influence of some foreign particle on the deposit in micrograph B, page 313. There something was deposited upon the metal which resisted the passage of the current, and hence the fan-like structure.

C. H. PROCTOR: I think I have answered more questions on "spotting out" this year than ever before in my experience. I recently received a letter from a firm that makes considerable art metal goods from brass and bronze mixtures, and they spoke about the "spotting out" problem. They had some bronze parts of some fancy lamps, I presume candles, cast perfectly plain; they had been copper plated and they "spotted out." They have been puzzled in so far as similar candles that came from the foundry and had never been near a solution had identically the same spots.

What was the cause of it? The gases that occlude in the metal when it is cast might possibly be hygroscopic in a sense, and absorb some moisture and cause "spotting out." That is what we get from the plating proposition. We believe it is due to the solutions getting into the pores of the metal and under the influence of the current, probably more or less. There is an entrance, but not an exit, and we cannot get it out. We think we have got it out, but when the work is finished and lacquered, it "spots out" just the same, but here is a case where it "spots" when it has never been near a solution.

O. P. WATTS[6] (*Communicated*): The physical weakness and brittleness of electrodeposited metals is well known. The method of alternate deposition described in this paper is novel, and, where heat treatment or mechanical working cannot be employed, appears a valuable means of obtaining heavy electrodeposits of superior strength.

[6] Asso. Prof. of Chemical Engineering, Univ. of Wisconsin, Madison, Wis.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# THE INFLUENCE OF THE ELECTRIC FURNACE ON THE METALLURGY OF NON-FERROUS METALS.[1]

By H. M. St. John.[2]

## Abstract.

The successful electric furnace, as used in brass foundries, rolling mills, and refining plants, is a machine for melting metal, operated by a mechanic who follows definite instructions. The man who issues the instructions and exercises general supervision over furnace operation should possess metallurgical skill and experience, but the operator need not necessarily possess either. As a result of its mechanical, semi-automatic nature, electric melting is gradually doing away with the secretiveness which has always characterized the non-ferrous industries, and is replacing the experienced brass melter by a mechanic who needs only to understand his machine and its capabilities. By its use of large melting units, with closed melting chambers which are virtually free from oxygen and products of combustion, electric melting has revolutionized metal-handling methods, and produces a more uniformly high quality of product, with less labor and less metal wastage, than have previously been possible of attainment.

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Non-ferrous metallurgy, as a matter of scientific control, has not thus far received the same attention which has been so widely accorded to the problems of ferrous metallurgy. The latter has been intensively studied and discussed in such detail that it is relatively easy to determine the influence which any given change

[1] Manuscript received July 27, 1921.

[2] Service Manager, Detroit Electric Furnace Co., Detroit, Mich.

in practice will have on the nature of the product and on the economy of the operations involved. The metallurgy of copper smelting and refining is also a matter of common knowledge among metallurgists, but the metallurgical problems involved in the manufacture and remelting of the alloys of copper, as practiced by foundrymen and secondary smelters and refiners, are so shrouded in mystery as almost to defy public discussion on a scientific basis.

Non-ferrous foundrymen are of two general classes, those who depend upon traditional rules, somewhat modified perhaps by their own experience, and those who are guided by scientific principles, worked out perforce in their own laboratories and plants, since the required data are not otherwise available. Both classes are highly secretive, the first because they imagine that their peculiar way of doing things comprises valuable manufacturing secrets, the second because the technical work through which they have developed and improved their methods really does give them a substantial advantage over their less well informed competitors and they can see no reason why information which has cost them time and money should be shared with others, less progressive, who have not seen the wisdom of working along similar lines and have nothing of value to give in return.

This is hardly the place to discuss the logic of either of the attitudes mentioned above, nor is it intended to speak slightingly of foundrymen who depend upon so-called "practical" methods to the exclusion of theoretical considerations. Many experienced foundrymen of this class achieve consistently good results, knowing only that certain metals, treated thus and so, will always behave in such and such a manner. But such knowledge, however valuable it may be, serves at best as nothing more than a well beaten path from which one cannot safely stray in search of new and possibly more fertile fields without some knowledge of the adjacent topography. Without more complete information as to the why and wherefore, progress tending toward improved and more economical methods, and toward a superior quality of product, must of necessity be slow and uncertain. Furthermore, one who has visited many foundries and talked to many foundrymen may well doubt whether the various kinks of the trade sometimes guarded so closely are really of value as secrets. These

things may be unknown to the novice but nearly all old foundrymen who are really skilled in their trade seem to know all about them.

There is also the brass melter who would like the world—and particularly his employer—to believe that the making of brass is a kind of magic in which he is particularly skilled and in which he excels his fellows to a degree which makes his services quite indispensable. As a rule his faith in his mysterious formulæ is quite as whole-souled and honest as that of the alchemist—whom he emulates and of whom he probably never heard—may have been a thousand years ago. A pinch of white powder—sodium bicarbonate is a favorite—introduced at just the right moment, will cause the metal in the crucible to pour perfect castings; a small quantity of a black powdery mixture, styled a "cleanser", brings all impurities to the surface of the metal, from which they can readily be skimmed. A cleanser of this nature which has been quite extensively peddled from foundry to foundry has, by recent analysis, been found to contain nothing more than coke dust and finely powdered silica. The works manager of a large manufacturing establishment using this "painkiller" in its foundry, apologetically remarked that he "didn't know what was in it but apparently it didn't harm the metal and it might do some good."

As a result of the generally prevailing conditions mentioned above it is difficult thus far to state in any detail what effect the electric furnace is having on the metallurgy of the non-ferrous metals, since the fundamentals of such metallurgy are so little understood in many plants where electric furnaces are in use, and so little discussed in others. One far-reaching influence of the electric furnace is, however, already apparent in its tendency to do away with secrecy, whether empirical or technical. This effect is due to the fact that the electric furnace reduces metal melting to a relatively exact basis, subject to mechanical control, and very little dependent upon the experienced eye or the "metal wisdom" of the melter. With the advent of the electric furnace, the old brass melter, who has served a novitiate and acquired a certain skill of hand and eye through years of experience, is giving way to a wide-awake mechanic, who knows little enough about brass but who is familiar with the mechanical and electrical

characteristics of the machine he is required to operate and can make it perform in any desired manner as directed by his superior. In plants under technical control, on the other hand, the metallurgist finds that most advantageous use of the electric furnace requires him to modify his previous practice and opens up new possibilities for improvement. In making these changes in his methods he naturally consults with the electric furnace manufacturer and with other metallurgists until presently he finds that he is taking from and adding to a common fund of information accumulated by all who are interested in applying the electric furnace to non-ferrous problems. In this way the electric furnace first renders obsolete rule-of-thumb secret methods which have been in common use and, in the second place, brings together the technical men who are interested in its use by adding to their secret technique a technique of its own which is not at all secret. As this tendency progresses it should be possible, in the course of a few years, to formulate the general principles underlying non-ferrous electrometallurgy in a much better fashion than is now feasible.

For the present one must be content with mentioning, without much attempt at detail, the changes which the electric furnace obviously is making in non-ferrous practice, hoping that the outline thus formed will be supplemented and amplified from time to time by those best qualified to furnish the needed information.

For convenience in discussion the melting process may be subdivided as follows:

Character of charge.

Method of charging.

Conditions to which metal is exposed during the melting operation.

Method of pouring.

Quality of product.

In discussing changes in practice which have been brought about, directly or indirectly, by the electric furnace, it is necessary to adopt some sort of standard as representative of the practice formerly in use, and for this purpose reference is made to Gillett's treatise on "Brass Furnace Practice in the United States"[3],

[3] Gillett, H. W. Brass furnace practice in the United States: Bur. of Mines Bull., No. 73, 1914.

published in 1914. Appearing, as it did, just prior to the commercial advent of the electric furnace, and summarizing comprehensively the practices then followed by most of the important American plants, it forms a very convenient basis for comparison.

## CHARACTER OF CHARGE.

The materials which are, or can be, utilized for brass furnace charges, may be listed as follows.

1. Virgin metals: copper, tin, lead, zinc, aluminum, etc.
2. Alloyed ingot.
3. Scrap metals: copper, aluminum, etc.
4. Heavy foundry scrap: gates, sprues, risers and rejected castings.
5. Light scrap: wire, stampings, sheet brass, etc.
6. Borings, chips, grindings, etc.
7. Concentrates.

Charges consisting wholly of virgin metal are, and always have been, rare. In fact some foundrymen maintain that satisfactory castings cannot be made from such charges, which is, of course, absurd. The chief objection is the high cost of the virgin metals, a factor which limits the use of all-new-metal charges to the manufacture of special castings for which a premium is charged. Such charges have always been considered somewhat more difficult to melt than charges consisting largely of previously alloyed metal, because of the necessity of stirring the zinc and other low-melting constituents into the previously melted copper. If the percentage of zinc is high the alloying process is also accompanied by a considerable loss of this volatile metal.

In those types of electric furnace which automatically stir the charge during the melting period the melting and alloying of new metals have been greatly simplified. All constituents of the charge, including the zinc, tin, lead, etc., are added at the beginning of the heat, the furnace is closed and the metal requires no further attention until it is ready to pour, at which time it is thoroughly alloyed and more thoroughly mixed than is ordinarily possible with hand stirring. Loss of zinc and tin is also greatly reduced. Charges consisting wholly of new metal can be melted in an electric furnace of this type with no greater loss than in

melting all-scrap charges. The consumption of electric energy, and the time required for melting, are not greatly increased.

The use of alloyed ingot is not so common in the electric furnace as it has been in various forms of fuel-fired furnaces. In electric melting practice metal losses are so small and so constant in value that all scrap produced in the foundry can be depended on as of correct composition, and it is a simple matter for any foundry to do its own alloying from new metals or from cheaper grades of scrap, as desired. Yellow brass rod chips, scrap tubing, clippings, etc., are frequently used as a means of introducing zinc into the alloy.

Scrap copper, aluminum, and lead are used in the electric furnace, very much as in the older forms of melting equipment. It has also been found that charges consisting entirely of scrap electrical copper can be used in making high-conductivity copper castings and wire bar, a result which could not formerly be obtained in any practicable way.

Heavy foundry scrap is used in electric-furnace charges in a manner not appreciably different from that which has commonly been practiced in other furnaces.

As already mentioned light yellow-brass scrap, such as stampings, clippings, etc., is frequently used in foundry electric furnaces as a source of zinc. Rolling mills have always utilized their scrap of this nature and are continuing to do so in the electric furnace. The tendency of the latter is to make even more desirable than before the cabbaging of light scrap since, in this manner, the desired weight of metal can be placed in the furnace at one charging and it is thus unnecessary to open the furnace for additional charging after melting has once started.

According to Gillett[4], the plants investigated by him in 1914 did not use more than 15 to 25 per cent. of borings in their regular charges. This practice has not changed to any great degree so far as fuel-fired furnaces are concerned. Excess borings are either run down into ingot and analyzed before use, or, in many cases, all borings are sold to a secondary smelter. As is well known, borings have a tendency to float after the rest of the charge has become molten and melt with great difficulty unless the bath is constantly rabbled. When in this state borings lose

[4] *Ibid*, p. 232.

zinc and oxidize badly because their surface is so large in proportion to their weight. In the open-flame or reverberatory furnaces there is the added danger that light chips may actually be blown out of the furnace by the blast or sucked out by the draft.

Here again the electric furnace so designed as to automatically stir its charge scores an advantage. By constantly submerging in molten metal the agglomerated mass of chips which would otherwise float on the surface, such a furnace melts this material as rapidly and efficiently as any other charge. In any well designed electric furnace the atmosphere is such that metal losses are greatly reduced, while in the "mixing" type of furnace charges consisting wholly of borings can be melted at a loss not greatly in excess of that experienced with heavy scrap and new metal. It is common practice in many foundries to run charges containing as much as 75 percent of borings and chips, using the metal in their regular casting production, whenever an accumulation of this material, or an advantageous purchase, makes such procedure advisable. Other plants now melt down their own chips into ingot in the electric furnace, instead of selling them or sending them to a smelter, as formerly.

Even concentrates are now used in regular electric furnace charges by many plants, in proportions as high as 30 to 40 percent of the total charge, these concentrates, of course, being relatively coarse and of a metallic content not below 85 percent. Leaner concentrates are being melted in the electric furnace and poured into ingot for analysis and remelt. While this practice is still in a somewhat experimental stage present indications are that finely divided concentrates, averaging as low as 60 to 70 percent metallic, can successfully be handled in this way. Concentrates obtained from the ashes of coal or coke furnaces contain metal from which zinc, tin and lead have been pretty well eliminated by vaporization and oxidation; practically speaking, only copper can be recovered from them. The same is largely true of metal which has been spilled in the pits of oil or gas crucible furnaces. The skimmings from open-flame oil or gas furnaces are also deficient in the white metals, while metal recovered from crucible skimmings is more nearly of the same composition as the alloy from which the skimmings were taken. Floor sweepings and worn-out molding sand contain metal of nearly standard

composition. Concentrates from these metal-bearing wastes are usually mixed indiscriminately so far as composition is concerned, being graded merely as to size of particles and richness of metallic content. Obviously these concentrates cannot easily be melted down in crucibles, since constant rabbling is required. They are commonly treated in direct-flame or reverberatory furnaces, in which, unless the metallic content is very high, such of the white metals as may still be present are finally lost and only the copper content recovered. Even the copper suffers from oxidation during this process.

In the electric furnace these concentrates, when they can be handled at all, can be melted in such a manner as to save nearly all of the white metal content. In the rocking indirect-arc furnace the necessary rabbling is accomplished mechanically and automatically, without human labor and without opening the furnace chamber. In any other type of electric furnace hand rabbling through an open door is necessary and much of the advantage peculiar to electric melting is thereby lost. The slag is the main problem to be dealt with in the electric melting of such materials. This is of minor importance in connection with high-metallic concentrates but in the handling of lower grades it is necessary to use a flux which will produce a thin slag, easily removed from the furnace and sufficiently fluid to permit the separation of small globules of metal which would otherwise be held in the slag and lost. It is upon the use of such fluxes, which, while performing the above function, must not at the same time attack the electric-furnace lining, that further progress in the electric melting of low-metallic concentrates depends.

From some of the foregoing it might appear that the tendency of the electric furnace is to make every foundryman his own smelter at the expense of the secondary smelter and refiner. To some extent this is probably true, but the electric furnace has compensating advantages for the latter also, when he chooses to adopt it for his own use. Many metal-bearing wastes, formerly purchased on a basis of their copper content, which alone could be recovered, can still be purchased on the same basis for smelting in an electric furnace which will recover a considerable portion of the white metals as well. Furthermore, the electric furnace takes care of the heterogeneous collection gathered in by the

junk man,—chandeliers, alarm clocks, cuspidors and cornets—in such a way as to deliver in the ingot a much greater percentage of the white metals than could formerly be salvaged. In this way the smelter who makes use of the electric furnace finds his profits greatly increased on the business to which he is justly entitled, even if he does lose some business formerly obtained from the foundryman who can now handle a larger percentage of his own scrap and wastes.

### METHOD OF CHARGING.

Fuel-fired furnaces do not lend themselves to rapid methods of charging. Even in large reverberatory furnaces the type of construction is necessarily such that the metal must be lifted from the floor level and shoveled or thrown by hand through a door in the front or side of the furnace. Two instances cited by Gillett, as reported to him by the furnace users, are illustrative. In one[5] it required three men's time for one hour to charge and make ready a reverberatory furnace handling a 3000-lb. charge. It required one man's time for two hours to melt the charge. In another case[6] three men were required for 1½ hours to charge a reverberatory furnace melting a charge of 8,000 to 10,000 lb. Some open-flame furnaces are so constructed as to permit of more rapid charging but such methods do not appear to be in common use. The charging of crucible furnaces, particularly those of the tilting type, is well known to be a laborious and time-consuming operation.

Certain types of electric furnace have been constructed with this point in mind; electric heat supply is inherently of such a nature as to make the problem a comparatively easy one. Even when the charge must be handled from the floor, 2000 lb. of metal can be thrown into an electric furnace in a maximum of 15 minutes, unless, as sometimes happens, portions of the charge are so bulky, or of such awkward shape, as to require separate handling of individual pieces. In electric furnaces so constructed as to permit charging through the top of the furnace, or through a charging door which is mechanically brought to that position, the use of a charging platform enables one to charge 2000 lb. of metal in as little as five minutes. The use of a bucket, or simi-

[5] *Ibid*, p. 88.
[6] *Ibid*, p. 90.

lar mechanical contrivance, where circumstances make the use of such a device practicable, reduces this time to three minutes or less. The writer personally observed one case in which 2000 lb. of bronze scrap and new metal was charged and the furnace again under power in one minute and fifty seconds from the time when the last of the preceding heat was poured.

In charging any brass furnace it is well recognized that the various elements of the charge should be placed in the crucible or furnace in a definite order. For example, it is common practice to charge chips, borings, etc., first, followed by ingot and heavy scrap, and finally by light scrap. This is done in order to facilitate rapid melting and reduce metal losses. The same practice is followed in electric furnaces, with some variations and one significant addition. It is customary in electric-melting practice to charge borings, or a part of the light scrap, first, followed by the white metals, then by the rest of the light scrap and the heavy scrap, and finally by any ingot, particularly copper ingot, which may be included in the charge. In the electric furnace the white metals, which in other furnaces must be charged after the rest of the metal is molten, are included in the original charge, and the disagreeable and expensive task commonly called "speltering" is eliminated. The saving of labor and metal thus effected is a very substantial one.

## MELTING CONDITIONS.

The conditions to which metal is exposed during the melting operation may conveniently be discussed under the following headings.

1. The application of heat.
2. The furnace atmosphere.
3. The furnace lining.
4. Slags, fluxes and covers.
5. Circulation of the metal.

### *1. Application of Heat.*

In direct-flame and reverberatory furnaces intense heat is applied directly to the surface of a shallow pool of metal, the lower portions of which must receive their heat by conduction from the directly heated surface. As a result this surface is necessarily

heated to a temperature substantially above that of the lower portions. The more rapid the melting speed the greater this heat gradient and the more excessive the superheat which the surface must receive before other parts of the bath are at a satisfactory pouring temperature. As a result, such furnaces show a high metal loss, both by oxidation and by volatization. Since, however, the application of heat is direct, the thermal efficiency is relatively high and the fuel consumption correspondingly low.

In crucible furnaces, whether pit or tilting, heat is applied to the walls of the crucible, through which it must be transmitted to the metal. Since the thermal resistivity of even a graphite crucible is quite appreciable the thermal efficiency of such furnaces is much lower than that of the direct-flame or reverberatory furnaces. On the other hand the metal is heated with a fair degree of uniformity and presents a relatively small surface—not heated above other portions of the bath—to the flow of furnace gases. These conditions make for a small metal loss and good quality of metal.

With one exception all commercial electric brass furnaces depend upon heat radiated from above to the surface of the metal bath. In certain types the heat is generated in a resistor so located that most of the useful heat must be reflected to the bath from the furnace roof, which thus acts as a secondary radiator, the bath itself being stationary as in the direct-flame furnace. In this case also the surface of the metal is, of course, superheated as compared with other parts of the bath, but, owing to the cleanly nature of electric heat and to the fact that the furnace chamber is closed, the metal loss is not necessarily high nor does the metal suffer oxidation. On the other hand, the refractories of which the roof is constructed, limit the rate at which heat may be applied to the metal, and, if the refractories are to enjoy a reasonably long life, the difference between roof temperature and the pouring temperature of the metal must be so little that the latter is not likely to be seriously overheated. This condition, however, makes for slow melting and a thermal efficiency which, for an electric furnace, is low.

In the moving indirect-arc type of furnace, heat is applied from an intense source to a metal bath of constantly changing surface. The arc is directly above the metal, although not in contact with

it, and the melting speed is very high, with a correspondingly high thermal efficiency. Since, moreover, all parts of the bath are constantly being tumbled into new positions by the mechanical motion of the furnace, no part is continuously exposed to direct radiation from the arc and no local superheating results. As in all successful electric brass furnaces, the furnace chamber is tightly closed against the admission of oxygen from without and the escape of metallic vapors from within. This condition, combined with the entire absence of local superheating, results in a low loss of metal by oxidation or volatilization.

In the one exception referred to, the melting heat is generated by the passage of induced electric current through the metal itself. In this furnace a slight superheat develops in the induction channel but since this superheating occurs at the bottom of the bath, with a considerable weight of cooler metal above, it does not result in serious loss of metal or in injury to its quality. This method of heat application is also highly efficient.

### 2. *Furnace Atmosphere.*

In all fuel-fired furnaces the furnace atmosphere consists of oxygen, nitrogen, unburned fuel, and the products of fuel combustion. Some excess of oxygen must be present if combustion is to be reasonably efficient, perfect combustion rquiring the presence of approximately twice the quantity of oxygen theoretically required to burn the fuel. On the other hand, the excess of oxygen must be kept at a minimum or serious oxidation of the metal will result. In practice a compromise is effected in an effort to keep the percentage of oxygen sufficiently low to avoid excessive oxidation and at the same time sufficiently high to accomplish as nearly complete combustion as possible. If the first object is achieved combustion is far from perfect and the flue gases contain unburned fuel in the form of soot, oil vapor, or combustible gas, if liquid or gaseous fuels are used, or soot and carbon monoxide if solid fuels are used. The products of combustion include carbon dioxide, carbon monoxide, water vapor and sulphur dioxide from sulphur in the fuel. Of these constituents oxygen and water vapor result in loss of metal by oxidation, while the resulting oxides and such sulphur dioxide as may be absorbed by the metal are decidedly injurious to its quality. In

this respect the crucible furnace is at a decided advantage as compared with direct-flame and reverberatory furnaces because of the much smaller surface of metal which it exposes to the furnace atmosphere.

In both the reflected-heat type of electric furnace and the electric arc furnace the atmosphere to which the metal is exposed is largely controlled by the presence of incandescent carbon in the resistors and in the electrodes. This carbon combines with the oxygen originally present in the closed furnace chamber to such an extent that free oxygen is practically eliminated before the metal becomes hot enough to oxidize. There is, however, a difference in atmosphere between the two furnace types. The ruling temperature of the resistance furnace is lower than that of the arc furnace, and in the former carbon oxidizes principally to carbon dioxide, with carbon monoxide present in perhaps half the percentage of carbon dioxide, nitrogen being the only other constituent present in any quantity. In the arc furnace the electrode tips are sufficiently hot to react with the carbon dioxide, forming carbon monoxide, which, except for nitrogen, is practically the only atmospheric constituent present after the first five minutes of the heat.

In either of these furnace types any moisture which may be present in the charge reacts with the incandescent carbon to form carbon monoxide, hydrogen and methane, with, possibly, fractional percentages of the higher hydrocarbons. Any oil which may be present in the charge "cracks" to form soot and various of the lighter hydrocarbons. Of the gases present in these furnaces, nitrogen, carbon monoxide and probably carbon dioxide, are ordinarily harmless, although the latter becomes oxidizing under certain conditions. We are then concerned only with the gases originating from the charge itself when it does not happen to be perfectly dry. Of these, hydrogen may be harmful but, under worst conditions, it is present in a much smaller proportion than is the case in combustion furnaces which produce water as one of the products of combustion. In cases where injury from hydrogen may be expected, it is probably important to make sure that the metal charged is reasonably dry. There is so far no reason to believe that methane or any of the other hydrocarbons which may be present have any effect whatever on the metal.

In the treatment of molten copper at high temperatures there is now excellent evidence to the effect that carbon dioxide and carbon monoxide will, to some extent, dissolve in the metal. Their elimination from the molten metal is, however, a relatively simple matter.

In the induction furnace, which contains no carbon parts, the oxygen originally present in the furnace chamber, will react with the metal unless some other means is adopted to eliminate it. For this reason a layer of charcoal on the surface of the metal is commonly employed in this furnace.

In general, the atmosphere of the electric furnace is, therefore, nearly ideal from a metallurgical standpoint. Oxidizing influences are absent, and sulphur dioxide is entirely eliminated except for such infinitesimal quantities as may result from sulphur present in the oil with which metal charges are sometimes contaminated. But this is not the whole story. The atmosphere of the combustion furnace is not merely oxidizing and otherwise injurious to the quality of the metal, but it is also a rapidly moving atmosphere of huge volume which carries with it up the flue considerable quantities of metal vapor, principally, of course, zinc. Gillett states[7] that various types of combustion furnaces emit flue gases varying in volume from 1550 cu. ft. to more than 6000 cu. ft. for every hundredweight of metal melted. This volume of gas, sweeping across the surface of the metal, removes the zinc vapor as fast as formed and maintains the vapor pressure of the zinc at practically zero, so that there is nothing to hinder continuous vaporization of the metal. Compare this with a 2000 lb. electric furnace having perhaps 25 cu. ft. of stagnant atmosphere above the metal, an atmosphere which rapidly builds up a pressure of zinc vapor equal to the vapor tension of the metal, after which further volatilization necessarily ceases.

As a result of all these factors, the electric furnace has unquestionably reduced the average metal loss of all the copper alloys commonly melted in it by a quantity equal to at least two percent of the metal charged. Clean yellow brass is electrically melted at a net loss between 0.5 and 1.0 percent, red brass at a net loss of less than 0.5 percent. While the accuracy of these figures is often questioned by those familiar with old brass-furnace methods

[7] *Ibid*, p. 138.

and unfamiliar with the new, and it must of course be admitted that higher losses are sometimes experienced in careless electric furnace practice or under unfavorable conditions, it has, nevertheless been established beyond question by many electric furnace users that the low figures mentioned above can be maintained in month-after-month operation. In discussing good brass-melting practice in combustion furnaces it is sufficiently accurate and entirely fair to say that the average net loss in such furnaces lies between two and three percent, in spite of the fact that in some plants and under some conditions losses as high as 8 to 10 percent are actually experienced. In speaking of electric furnaces it is equally accurate and fair to say that the average net loss lies between 0.5 and 1 percent, in spite of the fact that losses as high as 2.0 percent may sometimes occur.

### *3. Furnace Linings.*

Generally speaking, little is known about the metallurgical effect on copper alloys of the refractory materials commonly used in brass-melting furnaces. In the crucible furnace it is, of course, only the crucible which matters; trouble from this source is practically unknown. Open-flame furnaces are ordinarily lined with fire brick, essentially aluminum silicate with some free silica and alumina. Electric furnaces more commonly employ brick containing a high percentage of free alumina, one make of brick widely used for this purpose containing as much as 76 alumina and only 17 percent silica. There is a good deal of evidence to the effect that silica sometimes causes trouble in the melting of copper alloys, although such a small proportion as that mentioned above is harmless. Silica brick are probably unfit for any use which brings them in direct contact with superheated molten copper and its alloys. An opportunity exists for much improvement in the development of refractories for various electric-furnace applications, to insure in each case a material which will be at once durable and metallurgically suitable.

### *4. Slags, Fluxes, and Covers.*

The use of fluxes, or "cleansers", is not often necessary in electric melting since oxides are not formed during the melting process and there is no contamination from products of com-

bustion. If oxides or sulphur are present in the metal as charged, a small quantity of fluorspar flux is sometimes useful. Mention has already been made of fluxes for the purpose of producing a thin slag when concentrates are being melted in the electric furnace. Much progress is still possible along this line.

In combustion furnaces common salt is sometimes used to form a molten cover over the metal, to protect it from oxidation and keep back vaporization of zinc, particularly in the case of yellow brass. In the electric furnace a salt cover is useless and undesirable. Charcoal, commonly employed in fuel-fired furnaces, is used in electric-furnace practice in the induction furnace only. In arc and resistance types the incandescent carbon of the furnace itself effectively removes oxygen from the furnace atmosphere. As the induction furnace contains no carbon parts, charcoal, on the surface of its metal bath, serves to cover the metal with a film of mingled carbon dioxide and monoxide, protecting the metal from oxidation.

### *5. Circulation of Metal.*

Vigorous stirring of the metal during the course of the melting process is an innovation introduced by the electric furnace, if we except such rabbling of the metal by hand as has been practiced in the crucible and other combustion furnaces, laboriously performed only when the nature of the charge made such stirring absolutely essential. Reference is sometimes made to thermal circulation in the molten metal as having some tendency to keep the temperature uniform throughout the bath, but this circulation is so sluggish that, for practical purposes, it can be ignored. In the resistance electric furnaces, as well as in such stationary arc furnaces as are used for copper-alloy melting, hand-rabbling must be resorted to at times. In the moving indirect-arc furnace and the induction furnace, every charge of metal melted in the furnace is stirred vigorously by the furnace itself.

The principal advantage of this agitation of the metal unquestionably lies in the uniformity of temperature throughout the bath which is thus insured, resulting in more uniform metal, lower metal losses, and increased thermal efficiency. The thoroughness with which zinc and other alloying constituents

are mixed with the copper, without the uncertainties attendant upon hand stirring, is also a factor of great importance. There is some evidence also that a cleaner and more uniform quality of metal is produced in this way. One prominent rolling-mill which has adopted electric furnaces to the exclusion of all other forms of melting equipment, and, furthermore, using exclusively electric furnaces which possess this mixing characteristic, claims that the highest quality of brass can be produced only by the constant stirring of the metal which these furnaces make possible.

### POURING METHODS.

Metal melted in the crucible is, of course, carried in the original crucible to the sand moulds, billet moulds, or ingot moulds, into which it is to be poured. Metal melted in crucible-tilting furnaces, open-flame furnaces, or reverberatories, is poured from the furnace into ladles from which in turn it is poured into moulds. In all foundry installations this latter practice is followed with the electric furnace also, but in rolling mills it has become a nearly universal practice to pour directly from the electric furnace into ingot moulds, flat-metal moulds, etc., an arrangement to which the design of such electric furnaces as are used in rolling mills is excellently suited. In one large mill small electric furnaces are picked up by a crane and carried to the moulds but this is not likely to become common practice. A recent development is a systematic attempt to adapt the electric furnace for direct pouring into sand moulds, an attempt which, if successful, is likely to revolutionize pouring practice in the foundry.

Since metal melted in fuel-fired furnaces is not under very exact temperature control it has been customary in such furnaces to heat the metal to a temperature which the melter felt sure was hot enough, before pouring. As a result the metal taken from the furnace is nearly always too hot and must be cooled, before pouring into moulds, by the addition of small pieces of scrap, an operation commonly spoken of as "gating the metal down." This practice, although extravagant of fuel, tending to produce excessive metal loss, and liable to injury of the metal by overheating, is practically necessary in furnaces where the tempera-

ture of the metal cannot be accurately gauged in advance. In the electric furnace the rate of heat input and the quantity of heat applied to the metal during any given time are constantly being measured and recorded under the operator's eye so that the latter is always in a position to know the condition of his metal, without depending upon his skill for "judging temperature by eye" or even upon a pyrometer. Metal can always be poured at the desired temperature without the necessity of overheating to insure a margin of safety.

## QUALITY OF PRODUCT.

Whether the electric furnace does or does not produce a quality of brass superior to the best product of the crucible is still an open question. In foundry practice there is as yet very little definite evidence one way or the other. In the rolling mills there seems to be a definitely rising tide of opinion that the electric furnace does produce better brass than the best a v e r a g e which can be obtained from the crucible, judging both by their performance with normal rolling-mill charges. This much at least can be said: It is easier to produce a u n i f o r m l y high quality of brass in the electric furnace than it is in any type of combustion furnace. Metal losses are small and very uniform in amount so that a constant analysis is readily maintained; if a clean charge is used there are no particles of oxide to be entrapped in the metal and thus produce porous castings; the metal is not contaminated with sulphur or other products of combustion; the metal can be poured regularly at any desired temperature with remarkable exactitude. If the foundryman knows what pouring temperature will best suit the work he has in hand—which all too frequently he does not—the electric furnace makes it possible for him to duplicate this temperature invariably.

Nothing has so far been said in this paper about costs, nor is it the writer's prime object at this time to discuss this phase of the matter. But a discussion of the electric furnace's influence on foundry practice would not be complete without some mention of the way in which it is affecting the prospects of other melting furnaces, and this, in the last analysis, is a matter of dollars and cents. As compared with the crucible furnace, whether pit or

tilting, an efficient electric furnace of proper design produces at least an equal quality of metal at about half the cost. No attempt will be made here to prove this statement but the proof is in the hands of every plant which has used both types and much of the data supporting it has been published. Assuming that the statement is correct the crucible furnace is bound to be eliminated so far as approximately 90 percent of its present use is concerned. In the remaining 10 percent crucibles will still be used to melt diversified alloys handled in quantities too small to permit of efficient electric furnace use. The fact that in the electric furnace it is possible to produce brass of crucible quality in ton lots would in itself drive the crucible from what has been its principal stronghold, the rolling mill. In fact this process is already far advanced, as a trip through the principal brass rolling mills of the country will reveal to anyone who cares to investigate.

As compared with open-flame and reverberatory furnaces, the electric furnace produces brass at equal speed, of better quality and at two-thirds the cost. The tendency is to limit the use of these furnaces to low grade materials from which a low-priced product is to be made. Even in this field they meet with keen electric-furnace competition, wherever and whenever the cost of the fuel they use is high as compared with the cost of electric energy.

To summarize briefly, the electric furnace in the brass-melting industry has shown the following tendencies in its influence upon that industry.

1. A gradual breaking down of the secretiveness as to methods and results which has characterized this industry in marked degree.

2. The replacement of the experienced brass melter by a mechanic who may know next to nothing about brass but who can operate the electric furnace in accordance with instructions—just as he might operate any other semi-automatic machine.

3. The melting of high-quality brass and bronze in ton lots, or approximately ten times the amount of the average crucible heat.

4. The more convenient and economical handling of charges consisting wholly, or in large part, of new metals.

5. A more complete utilization by the foundry itself of chips, borings, grindings, concentrates and metal-bearing wastes.

6. A more complete recovery by the smelter and refiner of the metal contained in concentrates and foundry wastes purchased by him. Also a more efficient salvaging of junk metals.

7. Inclusion of zinc and the other white metals directly in the charge originally placed in the furnace, thus eliminating the laborious and expensive speltering process.

8. The introduction of mechanical charging methods, at a great saving of time and labor.

9. The elimination of fuel storage and handling, as well as the necessity of disposing of ashes and combustion gases. Brass foundries can now be built without stacks, while some who already have them are pulling them down.

10. Rapid progress in the determination of factors upon which successful brass melting depends, and which have previously been undetermined because of the inexact nature of the process.

11. Progress in the development of refractory and other materials needed by the electric furnace in order to produce the most favorable results of which it is capable.

12. The elimination of oxygen, sulphur and other contaminating elements, from the atmosphere to which the molten metal is exposed.

13. The melting of copper alloys at an average net loss of less than one percent, as compared with the two to three percent which was formerly considered good practice.

14. A reduction in the amount of hand labor necessary and an improvement in working conditions due to the more nearly automatic operation of electric furnaces.

15. A more exact temperature control which permits of nearly perfect duplication of results.

16. Rapid progress in the application of direct pouring from the furnace into moulds.

17. The production of a better average quality of metal than was formerly possible, even in the crucible.

18. A marked reduction in the overall cost of melting copper alloys, as compared with fuel-fired furnaces.

19. The rapid disappearance of the crucible from rolling mill work, and a somewhat more gradual reduction in its use elsewhere.

20. The gradual restriction of open-flame furnaces to a relatively narrow field of use.

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## DISCUSSION.

C. H. PROCTOR[1]: I would like to ask what is the comparative cost of the electric furnace as compared with gas or oil or the old-fashioned crucible method?

H. M. ST. JOHN: The comparative cost varies with the cost of fuel and electric power in different localities. On the average, including all items of expense, the cost of melting in an efficient electric furnace is about half that of melting in the crucible, and about two-thirds that of melting in direct-flame furnaces of large size, gas-fired or oil-fired.

Possibly if we had a few more brass melters present and a few less electric furnace men, it would start something.

H. W. GILLETT[2]: In bringing up to date the tabulation of electric brass furnaces in my paper at the last meeting of the Society, I found that those listed as to be installed at rolling mills have actually been installed, in spite of the industrial depression. That the rolling mills should carry out their previously made plans under such circumstances is pretty good proof that electric melting is economical for them.

ACHESON SMITH[3]: I would like to ask about the power question under these depressed conditions. Is the operator of such a type of furnace heavily penalized now by his arrangements for power, that is paying on his peak? Does it raise his cost of power per ton of metal very much higher than he had before?

H. M. ST. JOHN: As compared with normal times?

ACHESON SMITH: Yes.

[1] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.

[2] U. S. Bureau of Mines, Ithaca, N. Y.

[3] Vice Pres. and Gen. Mgr., Acheson Graphite Co., Niagara Falls, N. Y.

H. M. St. John: The instantaneous peak does not affect the power rate. So far as demand charge is concerned, it is somewhat easier for the furnace user to get concessions from the power company than formerly. Of course, the cost of power has increased slightly as compared with what it was, say two years ago.

F. A. Lidbury[4]: Is Mr. St. John in a position to tell us what the position of the average user of furnaces of this type is, in regard to his arrangements for power purchase? Is he, as a rule, able to get the power when and as he wants it, on a peak or other basis, or has he got to tie himself up on a long term contract for firm power which leaves little elasticity to correspond with business fluctuations? What are the general arrangements in this particular industry at the present time in that respect? In speaking of a peak basis, I mean daily peak.

H. M. St. John: You mean a contract which includes a clause dealing with off-peak use of the furnace, prescribing a certain period of the day—usually limited to part of the year only—when the user is not supposed to operate his furnace?

F. A. Lidbury: No; what I am driving at is this: In making his contract for power, does the brass melter have to tie himself up for practically the total amount of power that he uses when he is most busy for a period of years, so that he meets the question in depressed times as to how he is going to pay for the power he uses?

H. M. St. John: In no case, at least in none with which I am familiar. The actual condition is this: The user is sometimes required to sign a contract for three or five years, so that the power company may be assured that the cost of building a line to the user's plant will be returned to the company in the form of profits on the business. In most cases, during a business depression, it is possible for the user to have his furnace demand written off the books entirely for the time being, until he again operates his furnace, provided, of course, he contemplates a shut-down of several months.

J. A. Seede[5]: In discussing electric furnaces for melting nonferrous metals in 1920, I was told by a prospective customer that

[4] Works Manager, Oldbury Electro-Chem. Co., Niagara Falls, N. Y.
[5] Electrical Engineer, General Electric Co., Schenectady, N. Y.

his existing contract with the power company had such unusual provisions that if their total furnace load was divided among a number of smaller plants and the same total kw. hours were used in a given time, the total bill at the end of that time would be smaller than if it were all concentrated in one plant.

This is probably due to war-time conditions, when the power companies were endeavoring to conserve their power and have enough to supply all the customers, but it should not be permitted to handicap the electrothermic game in the future.

F. B. Steele[6]: Does the power factor enter into your furnace seriously and do you find the central stations object?

H. M. St. John: No. Some of the power companies specify that the customer's over-all load must maintain a specified minimum power factor; otherwise, the customer will have to pay a somewhat increased rate for power. The power factor of most electric furnaces is sufficiently high to exceed the prescribed figure.

E. L. Crosby[7]: This power factor situation you know more or less got in a bad way through the death of some of the early steel furnaces which obviously had very poor power factors; but as a matter of fact in most of the installations of any of the modern types of brass furnaces, I believe the power factor of the electric furnaces will materially benefit the over-all power factor of the manufacturing plant employing them. We found this to be almost universally true where a man has installed two, or three or four furnaces, if he has a power factor clause in his contract, he will probably benefit by the improved power factor at his distribution station because of the furnace installation.

H. M. St. John: In that connection, I might say that in a manufacturing plant, the over-all power factor is usually in the neighborhood of 70 to 75 percent. The electric furnace power factor is nearly always in excess of 85 percent, so that the electric furnace load does, as a rule, appreciably benefit the plant power factor.

[6] Asst. Gen. Manager, Utica Gas and Electric Co., Utica, N. Y.
[7] Vice Pres. & General Manager, Detroit Electric Furnace Co., Detroit, Mich.

G. K. Elliott[8]: Our plant entered the current period of depression with a number of oil furnaces and one electric furnace melting bronze. After a while the working time became uncertain; some weeks we were running for days and some only one. This condition made it difficult to run the electric furnace economically, and finally we had to discontinue it entirely because we were unable to work it enough to absorb the high maximum demand charge which it created. A season of business stagnation seems to furnish a condition under which the electric furnace is under a decided disadvantage. In our particular case, fortunately, we finally found some research work on several different kinds of metals, ferrous and non-ferrous, and placed the furnace again into service, but not on its regularly appointed production work.

[8] Chief Chemist and Metallurgist, The Lunkenheimer Co., Cincinnati, O.

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# MODERN DEVELOPMENTS IN THE BRITISH BRASS INDUSTRY.[1]

By Ernest A. Smith,[2] A.R.S.M., M.Inst.M.M.

Abstract.

The author presents the actual conditions of the British brass industry and its developments through the utilization of existing scientific and technical knowledge. A discussion is given embracing: electric brass furnaces in England; the extrusion, hot pressing and forging of brass; rolling mill practice; annealing; composition of industrial brasses; and treatment and utilization of scrap brass. [A. D. S.]

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A characteristic feature of modern industry is the preponderating part which scientific knowledge and methods play in its development. It is being increasingly recognized that one of the greatest factors in the progress of any branch of industrial activity is the extent to which scientific and technical knowledge is practically applied. This being so it is not too much to assert that the vigor and progressive spirit of an entire industry may well be gauged by the activity and growth of the individual firms engaged in it, and that this will depend in no small measure on the extent to which the individual firms avail themselves of the scientific and technical knowledge relative to their industry which modern research has placed at their disposal.

The very exceptional claims made upon manufacturers during the war period caused them to seek the aid of scientific knowledge and guidance to an unprecedented extent, and led to developments that would have taken much longer to accomplish under normal industrial conditions.

[1] Manuscript received August 31, 1921.

[2] British Non-ferrous Metals Research Assoc., Birmingham, England.

In few cases has such development been more pronounced than in the brass industry. Time-honored practices based largely on empirical knowledge, have been subjected to the closest scrutiny and modified or discarded where found to be incapable of meeting the demands of modern industry. Viewing the industry as a whole one cannot fail to recognize a great step forward towards greater efficiency in plant and improved quality of product. Signs are not wanting that the British brass industry is now entering upon a new era in its long history.

The conditions of modern works practice necessitate a large amount of scientific control, not only of raw materials, intermediate products, and finished output, but also of methods and appliances used. This fundamental factor enjoys today greater recognition and fuller appreciation than ever before, but in spite of the considerable progress that has been made it must be admitted that not a few manufacturers still regard science and research as things belonging essentially to test-tubes and laboratory experiments, and remotely removed from everyday works practice.

For an industry, so long established and so largely built up on empirical knowledge, such as the brass industry, to reconstruct itself on a scientific basis is, however, no light task, but all impartial observers are agreed that this change which began some ten years ago is now proceeding at an accelerated rate.

The rapid progress that has been made in non-ferrous metallurgical research during the past few decades has placed at the disposal of manufacturers a considerable amount of new information relative to the materials employed in industrial art. Research has afforded a much deeper knowledge of the structure of metals and alloys, and a better understanding of the phenomena which are met in connection with their use in industrial practice.

A comparatively large proportion of this research has been devoted to brass and kindred alloys. While it must be admitted that some of this new knowledge is of doubtful practical utility, and in some cases even misleading, there still remains a considerable amount of reliable knowledge that is of the greatest value and practical importance, when placed in the hands of a trained staff capable of utilizing it intelligently.

An example of a great benefit to the brass industry derived

from research is the electrolytic production of high-grade copper and zinc, both of which have done so much to improve the quality of brass products in modern times.

It would appear to be necessary to urge upon scientific contributors to brass literature the importance of giving to manufacturers much fuller information than is usually done on the history of the materials used in their researches. For example, one comes across many papers in which figures are given for alloys of various tensile strength, yield point, elastic limit, elongation, reduction in area, etc., but in how very few cases is there a really adequate history of the material tested. We frequently have reports for instance on rolled brass in which no mention is made of the degree of cold work that has been put upon it, or what, if any, heat treatment has been given. The brass industry in particular suffers from this lack of essential information.

It is the purpose of this paper to indicate briefly the extent to which existing scientific and technical knowledge has been utilized in the British brass industry as a whole, and to describe the development that has resulted from its utilization.

## WORKS LABORATORIES.

Undoubtedly, in the past, one of the obstacles to the introduction of scientific methods has been the lack of works laboratories, which would serve not merely the purposes of analytical control, but also act as channels through which new knowledge could find its way into the works. As an intelligence department the laboratory is invaluable, but to fulfill its purposes fully it should be constantly on the look-out not only for new scientific knowledge, but also for improvements in technical details of production.

The demand for ever increasing efficiency in the founding and manufacture of brass has led to the introduction of methods of determining the qualities of the materials used to a much greater extent than was formerly considered to be necessary. Not only is it absolutely essential to have an accurate knowledge of the composition of the metals used for alloying purposes, but also to make careful physical tests of the metal during the various stages of manufacture. It is also considered highly advisable to test most of the other raw materials used in the foundry and in other departments of the works. Although much has been

done in this direction there is still room for an extension of the system of putting the casting shop under the direct control of the laboratory, with an attempt to secure the most complete co-ordination.

The lack of laboratories is chiefly accounted for by the fact that in the brass industry as in other non-ferrous metals industries, there are comparatively few firms sufficiently large or wealthy to equip and maintain efficient up-to-date laboratories such as one finds in the steel industry. Groups of firms in association have established laboratories with suitable equipment, so as to be in a position to exercise more exact control of materials used, as well as of quality of products manufactured.

The first co-operative laboratory started in Birmingham in 1916 took the form of a small company, registered under the Board of Trade, and limited by guarantee. The equipment consists of a complete chemical laboratory fitted with every necessary appliance, together with a metallographic laboratory and appliances for physical testing and for pyrometric work. With such equipment many of the minor problems that present themselves in every-day works practice can be investigated and assistance given to the individual firm in whose works the difficulty arose.

### MELTING AND FOUNDRY PRACTICE, COKE AND GAS FIRED FURNACES.

Manufacturers are today more fully appreciating the fundamental importance of a sound ingot as the primary step to the successful and economic manipulation of the material in subsequent operations.

As H. B. Weeks has so well pointed out[3] "the architectural designs of a workshop have much more to do with its efficiency than is generally supposed. Particularly does this apply to foundries where fumes, smoke, and dust are continuously mingling with the atmosphere in which the moulders have to work. It is on that account, therefore, essential that spacious, well-lighted, well-ventilated, and lofty buildings should be erected for foundry purposes."

Many old brass foundries have been altered and remodelled as far as possible on modern lines, and newly erected foundries

[3] Journal Institute of Metals, 1920. **24**, 76.

have been carefully planned with due consideration to the various factors mentioned. But much yet remains to be done to bring the foundries and melting shops of the brass industry as a whole to that state of efficiency in design and equipment, which is so essential to its future well being and progress. The substitution of up-to-date appliances for old, and the extension of labor saving devices are important factors in improved foundry production, and these factors are not being lost sight of where economic conditions are favorable to their adoption.

The furnace being of primary importance in foundry work has received a considerable amount of attention during the past decade. The old simple form of square coke-fired crucible furnace, almost universally in use at the beginning of the present century, has now been largely replaced either by improved types of coke-fired furnaces or by gas-heated furnaces. Whilst gas furnaces offer several important advantages over coke furnaces, and are being employed in increasing numbers for melting brass, it cannot truly be said that they are fully established for brass melting generally. The modified coke fired crucible furnace is still the most generally employed for melting brass and other copper alloys.

The ordinary type of pit coke fired crucible furnace has however been much improved and made more efficient by alterations in design, chiefly in the introduction of new forms of bottoms which permit of a more satisfactory supply and distribution of the air, which in some cases is preheated. A number of fire clay furnace bottoms have been patented, such as the Wigley, Edgar Allen, Hall, etc. A number of furnaces with bottoms of this type are in use, and are found to be much more economical and efficient and a great improvement over the old pattern furnace bottoms. Attention has also been given to the construction of the furnace lining and the quality of the material of which it is made. Another form of furnace in fairly general use is Carr's patent furnace, in which provision is made for retaining the heat by inserting non-conducting material in the furnace lining; special facilities are also made for a good supply of air, and for cleaning. At the brass foundry of Messrs. Vickers, Ltd., Barrow-in-Furness, there are forty-four crucible furnaces of a modified Carr type, which are stated to have contributed in no small

measure to the success of the foundry work. Plumbago crucibles of 300, 200, and 150 lb. holding capacity are used.

With regard to gas fired crucible furnaces these have been applied to certain classes of brass melting in many localities where coal gas can be obtained for heating purposes at a reasonably low rate. Many types of gas furnaces having crucible capacities from 50 lb. to 800 lb. have been introduced for brass melting, and may conveniently be divided into two main classes according to the manner in which the gas is applied, viz.: low pressure furnaces and high pressure furnaces.

The low pressure type of furnace usually consists of pit furnaces and tilting furnaces with a crucible capacity of from 60 to 800 lb. which are employed for melting all classes of brass for the production of castings, ingots, billets, and strip and for melting scrap and swarf.

The high pressure type consists of pit furnace with a crucible, capacity varying from 60 to 200 lb. for melting brasses for strip and billets and for sand castings.

For this class of work furnaces fitted with atmospheric injector burners are generally used except where high speed of melting is required. Where gas furnaces have been introduced for brass melting they are chiefly of the low pressure type, as in the majority of operations there is no need to use high pressure gas.

In Birmingham, the center of the British brass industry, the Corporation has twenty miles of high pressure gas main laid and several brass founders in the city have adopted high pressure gas furnaces. A serious objection to all gas furnaces working under pressure is the noise, which is very trying to the melters and tends to militate against efficient production.

The author is in agreement with S. W. Brayshaw and others in considering that the future of gas melting furnaces lies not in high pressure gas, nor even with gas from the main, and air at 1 or 2 lb. pressure, but with ordinary gas and air at only a few inches of pressure not exceeding a 12-inch water column. This would mean an enormous cheapening of cost, owing to the economy of plant, since one would use merely a rotary fan. Such furnaces would be far less noisy to work.

It is now generally agreed that the working costs of the gas-fired furnace, under works and not test conditions, can be equalled

by an ordinary well-designed coke-fired plant, and particularly by installation of the square-furnace type, such as have given good results in Birmingham and elsewhere. The advantages claimed for gas-fired installation, such as increase of output and longer life of crucible, appear to be offset in works practice by the breaking down of the furnace refractories under the influence of local heating of the latter in gas-firing, a lack of uniformity in heat distribution, and the risks of absorption of gas during melting operations. The pouring temperature has a great influence on the consumption of gas and another cause of wide difference in the melting figures for the same metal is its physical state. Thus the more finely divided the metal the more gas is required for melting. Usually ingots and heavy scrap are the easiest to melt whilst light scrap and swarf may require double or treble as much gas as ingots.

The choice of furnace for brass melting is largely regulated by the class of work to be done. For comparatively light castings of varying weight and composition the coke or gas-fired pit furnace is generally preferred, but for large quantities of metal of uniform composition required at regular intervals for heavy class work the tilting furnace, either coke or gas-fired, is found to be more efficient and economical, owing to the lower fuel consumption, longer life of crucible and less labor required. The crucible capacity for small size tilting furnaces is usually about 120 to 150 lb., but the larger furnaces have a maximum capacity of 1000 to 1200 lb. Crucible tilting furnaces of relatively large capacity, developed during the ten years previous to the outbreak of war, found extensive use during the war period. So far was this the case that taking into consideration the tilting furnaces existing before the war together with those installed for war work, it is probable that about one-third of the total annual output of brass in recent years was melted in tilting furnaces. The average all-round working heat efficiency of the coke-fired crucible tilting furnaces on 70:30 brass is stated to be about 15 percent. Pre-heaters are attached to most of the modern crucible furnaces in use both for pre-heating the metal charge and in some cases the air supply.

Reverberatory or air furnaces capable of melting several tons of metal are in use where large quantities of metal are required

for heavy castings. These are usually coal-fired, but the application of gas-firing is receiving attention and has been adopted in some cases. For large quantities such furnaces are more economical and speedy to use than a number of smaller furnaces, and give a product more homogeneous in composition. When several small furnaces are used it is difficult to collect the pot charges into a ladle, and keep the metal warm enough for casting.

### ELECTRIC FURNACES IN GREAT BRITAIN

The application of electrical energy for melting brass and other copper alloys offers many advantages, and the development of furnaces of this type on the Continent and in America is being watched with great interest. So far the high cost of power has done much to delay more adequate attention being given in England to electric melting, but there is little doubt that a substantial reduction in electric power costs will bring these furnaces into greater prominence.

Owing to the comparatively low temperatures involved in melting most non-ferrous metals and alloys as compared with iron and steel, the electric furnace has not yet, on financial grounds, justified its employment for brass and similar alloys, except when dealing continuously with comparatively large quantities of material of uniform composition. The accurate control of working temperature and atmosphere, however, which the use of electric furnaces confers appears to mark it as one of the furnaces of the future.

Electric furnaces of the resistor type, in which a crucible is either heated externally or itself acts as the resistor, appear to be the type that appeals most to the brass melter, especially if provision is made for lifting the crucible out of the furnace to permit of hand-casting. Several forms of transformer furnaces for melting brass have been developed in England and on the Continent, and in this type the carbon crucible acts as the resistor to the passage of the alternating current and thus generates the necessary heat. This type of furnace is preferred because it conforms to the more varied requirements of general brass foundry practice, where usually comparatively small quantities of a number of alloys of different compositions have to be handled. Several furnaces of this type with a capacity up to

100 lb. or more of metal have been introduced in recent years and are being experimented with at several works. In cases where large quantities of one or two particular alloys only have to be dealt with, and for the melting of scrap, etc., electric furnaces of large capacity up to one-half ton or more are in use, but are so far in the experimental stage.

There would appear to be comparatively little scope in the British brass industry for electric furnaces of large capacity such as the Ajax-Wyatt, Detroit Rocking, and the Baily, in which the bulk of the electric brass melting has been done in America. These furnaces require large and expensive installation and must be operated continuously on one or at most two standard alloys before any material saving can be shown. These conditions do not apply to a large majority of the British works, many of which have only an average monthly output of from 500-600 lb. or even less and are called upon to supply such a variety of alloys and products that they cannot economically operate a furnace of one-half to one ton capacity continuously.

In addition to the introduction of newer types of furnaces considerably more attention has been given in recent years to details of casting technique, such as temperature of the metal, rate of pouring, dressing of moulds, etc., all of which are important factors in the production of sound metal. In this connection mention must be made of the use of the fireclay dozzle or feeder head which has been strongly advocated by W. R. Barclay and others during the past five years, for the production of sound ingots as free as possible from pipe. As is well known such dozzles have long been used in crucible steel casting and have done much to render the "feeding" of the molten metal into the ingot mould more efficient.

The hot dozzle inserted at the top of the ingot mould acts as a small secondary crucible holding the metal in the liquid state at least sufficiently long to allow it to be drawn into the interior of the ingot as required by the shrinkage cavity.

Where the feeder head has been introduced it has been of considerable assistance in producing sound brass ingot metal. The usual method of pouring adopted by the brass caster differs however from the steel caster's method and militates against the use of the feeder head, consequently when the non-ferrous metal

caster employs the feeder head he must conform more closely to the steel caster's method. An objection sometimes urged against the use of the dozzle is that it can only be used once and is then scrapped, but although this is the case experience has shown that the initial cost of the dozzle is invariably covered by the larger percentage of sound ingots that result from its intelligent use.

With regard to general foundry work some type of moulding machine is now almost universally employed for repetition work in which large numbers of duplicate castings are required. There has been a considerable extension in the use of moulding machines during the past few years and in this respect British manufacturers are indebted to American inventors for many of the most serviceable machines in use.

## EXTRUSION OF BRASS.

Closely allied to the casting of brass is the shaping of the metal by the extrusion process in which the hot metal, while in a more or less plastic condition is forced by heavy compression through a die, from which it "extrudes" in the form in which the die has been cut.

In no section of the brass industry has development been more rapid in recent years than in the production of rods and sections by the extrusion process, which was invented by Alexander Dick and developed by the Delta Metal Co., Ltd. Before the war the extrusion process was little known apart from one or two British firms who had specialized in the process and brought it into almost everyday use. The methods adopted were jealously guarded and the knowledge of the process in actual practice was confined to only these few firms. As a result however of the imperative demand for a large and rapid production of brass bars, extrusion presses were fitted up and installed in many works to meet the demand; with the result that the use of extruded bars and sections received a great impetus. A number of firms having equipped their works with the necessary machinery for the process are now actively interested in the production of extruded material, and are giving the industry the benefit of their equipment and experience so that a considerable quantity is now being produced for industrial purposes. The

demand for suitable presses for extrusion has been well met by British engineers, who supply hydraulic plant with 600 to 1000-ton presses, capable of extruding brass bars up to 3 inches drawn from standard billets of 5.25-inch diameter by 24 inches long. Amongst the more prominent makers of extrusion plant are Messrs. Fielding & Platt, Ltd., of Gloucester, Henry Berry & Co., Ltd., Leeds, and Davy Bros., Ltd., Sheffield.

Brass of the ordinary 60:40 composition is most suitable for strong extrusion work and is the most widely used alloy, being soft and easily extrudable when hot. When alloys of other compositions are used they have to be governed by their capacity for "flowing" when heated for extruding. With an increase in the copper content the metal becomes harder and more difficult to extrude. A 600-ton press will satisfactorily deal with brass up to about 62 percent, but larger presses are required for extruding metal of higher copper content.

Special brasses containing small percentages of other metals such as iron, manganese and aluminum to give additional strength are also being extruded satisfactorily, the added metals having but slight effect on the extruding properties provided due regard is paid to the quantity added. The extrusion process has many advantages over the older methods of rolling and drawing, and there is every prospect that the process will be considerably extended in the future.

The ease with which sections, many of which are very complicated, can be produced by the process, practically to size, at one operation, together with the fact that sections can be extruded that would either be impossible or extremely difficult to produce either by rolling or drawing, no doubt largely accounts for the increased favor which the products of this method of manufacture are finding.[4]

The making of tubes and hollow sections is included in the newest applications of the extrusion process, the difficulties at first encountered in their production having now been successfully overcome.

So far as the manufacture of solid drawn brass tubes by the ordinary process of drawing is concerned there is little advance to be recorded in the actual appliances used, but manipulation

[4] Metal Industry, No. 19, 1920, 17, 404.

has been modified in the light of modern research especially in its relation to season-cracking, to which brass tubes drawn through a die are somewhat susceptible.

## HOT PRESSING AND FORGING.

Another section of the brass industry that has developed greatly during recent years, and is today of considerable industrial importance, is the manufacture of light parts by the process of pressing a heated billet to a definite shape in suitable dies. In some cases the metal is stamped cold but the more general practice is to heat the metal to a suitable temperature before subjecting it to pressure. Brass of 60 : 40 composition has been found in general practice to give the most satisfactory results owing to its good forging qualities, but brass of other compositions is also employed.

Extruded rod is extensively used as raw material, though cast bar is used in many cases. The pressures employed vary from 70 to 400 tons, although 200 tons available pressure is capable of dealing with a large number of the articles manufactured in brass. The most suitable temperature for the hot-working of brass varies with the composition, and has been the subject of recent research. "It would appear that the work done during compression diminishes with increasing temperature from 500° C. onwards, at first rapidly and then more slowly. For copper, the work required at 800° is about one-third of that required at 500°, and the influence of temperature becomes more strongly marked in alloys containing 12 or 15 percent of zinc. For brass with 28 percent of zinc, the work at 800° is one-quarter of that at 500°, and for brass with 37 percent of zinc, one-tenth. In the last case three times as much work is required at 700° as at 800°. As soon as the $\beta$ phase makes its appearance the work becomes less, and with 42 percent brass may be compressed at 500°, and the full softness is reached at 700°. $\alpha$ brasses are therefore best worked at 800° C., higher temperatures being undesirable on account of burning. At this temperature, all the alloys examined undergo the compression of 50 percent without cracking. Most of them have been compressed 80 percent without cracking. The work required at all temperatures increases with increasing zinc content to a maximum

at 15 percent of zinc and then rapidly diminishes to a very small value in the $\alpha$ $\beta$ region."[5]

The speed of working and the flow of the metal are important considerations in hot-pressing. The advantage of the die-pressing process is that the piece being produced under heavy pressure, is very close grained and free from the defects such as blow-holes and pin holes, not infrequently met with in brass castings. They also have a smooth surface and no hard skin as in castings, and require little or no machining.

The machineability of brass is a matter of great importance, and has received a large amount of attention during the war period. Among the most important investigations on this subject may be mentioned that by C. H. Desch who conducted experiments to ascertain why brass rods of approximately 60:40 composition had been found to give widely differing results on machining. He found that the presence of small percentages of metals other than copper and zinc changes the relative proportion of the *alpha* and *beta* constituents, and that the most desirable structure for machining purposes was an arrangement of fine fibrous *alpha* crystals separated by a comparatively small quantity of *beta*. This could be obtained by the employment of an alloy containing as nearly as possible 40 percent "apparent" zinc, *i.e.*, with the added metals calculated to the equivalent quantities of zinc, and by the use of moderate temperatures and powerful presses in extrusion of the rods. It was found that brass of good machining quality should contain as nearly as possible 60 percent of copper and 1.5 percent lead, with a minimum percentage of other metals.

## ROLLING-MILL PRACTICE.

Although there is no marked advance in brass rolling mill practice, a number of mills of improved design have been installed during the past ten years and better work is being produced than formerly.

Both in England and in America there is need for a much

[5] Journal Institute of Metals, 1921, **25**, 398

closer study of the factors which tend to soundness of ingots, which is of such vital importance in the production of sheets of high-grade quality.

The production of a superior finish to sheet brass is not however altogether a question of a sound ingot or of good rolls, important as these factors are, but is to a large extent dependent on the exercise of scrupulous cleanliness in all the details of the rolling operations. It would appear to be in this direction that improvement in British rolling practice is to be sought. One important factor that operates against the British sheet brass roller is that he is not generally able to confine his rolling to comparatively large orders of one class of material which are so conducive to economic production, and which pertain to most Continental rolling mills. More frequently he is called upon to supply small quantities of material varying in composition and gauge, which adds considerably to the cost of rolling and militates against superior finish when the same rolls are used for all classes of work. The speed of rolling varies with different manufacture and whether the metal is hot or cold rolled. The generally recognized speeds for cold rolling are approximately as follows:

| | Ft. per Min. |
|---|---|
| Breaking down strips | 20 to 40 |
| Finishing sheets | 60 to 80 |
| Finishing sheets | 80 to 100 |
| Finishing rods | 100 to 120 |

The amount of reduction given depends upon the material and the temperature of annealing. On breaking down mills of large sizes for non-ferrous metals generally very heavy pinches have been employed, being in some cases as much as ½-inch, but a common practice is ⅜-inch. In the later stages reduction from 2.5 to 1 gauge is still general. It is to be regretted that so little reliable data on the best conditions for brass rolling have been published. Present day British practice is to a large extent based on empirical knowledge and there is urgent need for systematic research into all the factors governing the best economic operative conditions for rolling the industrial brasses, such as percentage reduction, number of passes to obtain given reduction, speed of rolling, amount of pinch in the initial stages, temperature

of hot-rolling, etc., all such factors being studied in connection with the temperature and time of annealing.

## ANNEALING.

For annealing purposes gas-fired furnaces of the close annealing type have been largely introduced in place of the old open bed coal-fired furnaces, and the temperature controlled by pyrometric observations in compliance with the more exact knowledge on heat treatment resulting from modern research. The installment of modern furnaces has considerably lessened oxidation during the annealing process and in consequence reduced the cost of manufacture through obviating the necessity of removing excessive scale. In this connection it may be pointed out that in several instances salt baths have been introduced for annealing small brass articles with considerable success and reduction in finishing costs.

The average gas consumption per 100 lb. of metal annealed, including gas used for preliminary heating of the furnace, and town gas of net calorific value of about 500 B.T.U. is given by Hartley as follows:—

| Nature of Work | Gas Consumption in Cu. Ft. per Cwt. Metal Annealed |
|---|---|
| Light brass stampings | 100 — 125 |
| Heavy brass stampings | 150 — 200 |

The temperatures employed for annealing, and the time required to complete the operation, are of course dependent on the composition and nature of the metal to be treated, but it may be stated that much closer attention is now being given to this operation, with the result that there has been a considerable improvement in the subsequent mechanical treatment and finishing of the material.

## COMPOSITION OF INDUSTRIAL BRASSES.

The figures given in the accompanying Table I may be taken as representative of the composition of the bulk of the ordinary brasses now being manufactured for industrial purposes, and of which thousands of tons are prepared annually. The extended use of brass for engineering and electrical purposes in recent years has resulted in a considerable development of the brass

trade, but now that the enormous demands for brass for war purposes has ceased, manufacturers are earnestly seeking new uses for the metal so that production may not have to be curtailed.

TABLE I.

*Approximate Composition of Brasses.*

| Trade Names | Percent | | Uses |
|---|---|---|---|
| | Copper | Zinc | |
| Brazing Metal ..... | 66-67 | 34-33 | |
| Brass for extrusion and hot-pressing ..... | 60 | 40 | |
| Brown Metal ..... | 87-88 | 13-12 | For buttons, badges., etc. The metal polishes to a golden color. |
| Cap Metal ..... | 97 | 3 | For shell-caps. |
| Best English Brass (Cartridge Metal) .... | 70-72 | 30-28 | For deep stamping and drawing, brazed tubes, etc. |
| Dipping Metal ..... | 73-74 | 27-26 | For articles that require strong brazing or hard soldering. |
| Enameling (Tombac Gilding) .... | 92-93 | 8-7 | Used in jewelry and art metal trades. Enamels well. |
| Gilding Metal ..... | 90-91 | 10-9 | |
| Ordinary Brass (Yellow Metal) (Muntz Metal) ..... | 60-62 | 40-38 | Sheets, tubes, etc. |
| Princess Metal Tombac Brass, (Similor Metal)..... | 81-82 | 19-18 | Sheet, wire, etc. |
| Solder ..... | 50 | 50 | |
| Stamping Metal ..... | 65 | 35 | High class deep stamping alloy. |
| Turbine blading ..... | 70 | 30 | For low pressure steam. |
| Wire Brass: Ordinary Brass Wire.. | 62-63 | 38-37 | Weaving, cutting up in automatic machines, etc. |
| Better quality ..... | 64-66 | 36-34 | |
| Brazing Wire ..... | 70 | 30 | |
| Solder ..... | 73 | 27 | |
| Union Wire ..... | 75-81 | 25-19 | |
| Gilding Wire ..... | 90 | 10 | Used by weavers in fine sizes. |
| Spring Wire ..... | 95-98 | 5-2 | |

Considerable attention is being given to the development of the so-called high tension brasses for engineering purposes in which enhanced properties are conferred on ordinary brasses by the addition of comparatively small quantities of metals such as nickel, manganese, aluminum, etc. Many of these are very com-

plex in composition and the exact influence of certain added metals is not completely understood, and their presence in some cases is of doubtful utility. To obtain the best results with these special brasses, improved knowledge of the true effects of the added metals is desirable so that endeavors may be made to simplify their composition.

The main object sought in the addition of other metals in commercial complex is to produce alloys, which, in the cast state, have a much improved yield point and maximum stress and increased hardness, with at least no serious loss of ductility; and, when

TABLE II.

*Composition of Special Alloys.*

| Alloy | Cu | Zn | Sn | Pb | Fe | Mn | Ni | Al |
|---|---|---|---|---|---|---|---|---|
| Aich's Metal ..... | 60.0 | 38.0 | ... | ... | 1.8 | ... | ... | ... |
| Sterro Metal ..... | 55.5 | 42.0 | ... | ... | 2.5 | ... | ... | ... |
| Sterro Metal ..... | 55.0 | 42.4 | 0.8 | ... | 1.8 | ... | ... | ... |
| Delta Metal ..... | 60.0 | 35.5 | 1.75 | 1.4 | 0.75 | ... | ... | ... |
| Delta Metal ..... | 55.0 | 43.5 | ... | 0.4 | 1.1 | ... | ... | ... |
| Delta Metal ..... | 58.3 | 39.0 | 0.06 | 0.15 | 0.13 | 0.14 | 2.2 | ... |
| Manganese Bronze.. | 69.0 | 24.2 | ... | 1.6 | ... | 0.25 | ... | 4.9 |
| Manganese Bronze.. | 58.5 | 38.5 | 1.4 | ... | 1.6 | 0.02 | ... | ... |
| Manganese Bronze.. | 56.2 | 40.5 | 1.2 | 0.4 | 0.4 | 1.1 | ... | 0.2 |
| Manganese Bronze.. | 56.0 | 39.6 | 1.2 | ... | 1.1 | trace | 2.0 | 0.1 |
| Manganese Bronze.. | 54.9 | 41.7 | 1.4 | ... | 1.2 | 0.5 | ... | 0.4 |
| Aluminum Brass.... | 61.0 | 35.3 | ... | ... | 1.0 | 0.5 | ... | 1.5 |
| Iron-Nickel Brass.. | 54.1 | 38.0 | ... | 0.42 | 2.5 | 0.9 | 3.6 | 0.4 |

rolled and forged, a still greater improvement in mechanical properties, as shown by tensile tests. It is difficult, however, to say exactly how much of such improvements are due to any particular added metal. Heat treatment is advocated in some cases, but experience appears to show that it lowers the elastic limit, and not as in the case of steel actually raises it. The complex composition of the special brasses in general use is illustrated by the examples collected in Table II, by O. F. Hudson. Examples of mechanical tests obtained with these alloys are also given in Tables III and IV.

In addition to these it may be mentioned that several firms that

## TABLE III.

*Mechanical Tests of Special Alloys.*

| Alloy | Composition | | | | | | | Tensile Tests | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Fe | Mn | Ni | Al | V | Condition | Yield Tons Sq.In. | Max. Stress Tons Sq. In. | Elong. Percent on 2 in. | |
| Delta Metal ..... | ... | ... | ... | ... | ... | ... | ... | Square bar annealed.... | ... | 27.8 | 38 | Law |
| | ... | ... | ... | ... | ... | ... | ... | Flat plate annealed..... | 12.1 | 30.0 | 36 | " |
| | ... | ... | ... | ... | ... | ... | ... | Flat plate ..... | 13.7 | 35.4 | 14 | " |
| | ... | ... | ... | ... | ... | ... | ... | Round bar ..... | 23.4 | 32.1 | 23 | " |
| | ... | ... | ... | ... | ... | ... | ... | Hexagonal bar ..... | 25.0 | 31.3 | 11* | " |
| Manganese Bronze... | 58.8 | 38.1 | 0.8 | 0.7 | ... | 1.2 | ... | Cast (?) ..... | 13.6 | 24.2 | 22 | Norris |
| Manganese-Vanadium Bronze ..... | 58.6 | 38.5 | 1.0 | 0.5 | ... | 1.5 | 0.3 | Cast (?) ..... | 22.6 | 36.4 | 12 | " |
| Vanadium Bronze ... | ... | ... | ... | ... | ... | ... | ... | Cold drawn, 5/8 in. rod.. | 35.7 | 41.1 | 11.5 | " |
| Nickel-Iron Brass .. | 54.1 | 38.0 | 2.5 | 0.9 | 3.6 | 0.4 | Pb 0.4 | Chill cast ..... | 13.2 | 32.5 | 43 | Millington |
| | | | | | | | | Sand cast ..... | 11.6 | 23.7 | 13.5 | " |

* Broke in ext. mark.

## TABLE IV.

*Mechanical Tests of Special Alloys.*

| Alloy | Composition | | | | | | | | Tensile Tests. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Sn | Pb | Fe | Mn | Ni | Al | Condition | Yield Pt. Tons Sq.In. | Max. Stress Tons Sq. In. | Elong. Percent on 2 in. | Reference |
| Delta Metal ..... | 60.0 | 35.5 | 1.75 | 1.4 | 0.75 | ... | ... | ... | Square bar annealed.. | ... | 27.8 | 39 | Law |
| | 55.0 | 43.5 | ... | 0.4 | 1.1 | ... | ... | ... | Flat plate annealed... | 12.1 | 30.0 | 36 | " |
| | 58.3 | 39.0 | 0.06 | 0.15 | 0.13 | 0.14 | 2.2 | ... | Flat plate ..... | 13.7 | 35.4 | 14 | " |
| | ... | ... | ... | ... | ... | ... | ... | ... | Round bar ..... | 23.4 | 32.1 | 23 | " |
| | ... | ... | ... | ... | ... | ... | ... | ... | Hexagonal bar ..... | 25.0 | 31.3 | 11* | " |
| Manganese Bronze | 58.8 | 38.1 | ... | ... | 0.8 | 0.7 | ... | 1.2 | Cast (?) ..... | 13.6 | 24.2 | 22 | Norris |
| Manganese-Vanadium Bronze ... | 58.6 | 38.5 | ... | ... | 1.0 | 0.5 | ... | 1.5 | Cast (?) ..... | 22.6 | 36.4 | 12 | " |
| Vanadium Bronze. | ... | ... | ... | ... | ... | ... | ... | ... | Cast ..... | 12.1 | 31.7 | 32 | " |
| | | | | | | | | | Cold drawn 5/8 in. rod. | 35.7 | 41.1 | 11.5 | " |
| Nickel-Iron Brass. | 54.1 | 38.0 | ... | 0.4 | 2.5 | 0.9 | 3.6 | 0.4 | Chill cast ..... | 13.2 | 32.5 | 43 | Millington |
| | | | | | | | | | Sand cast ..... | 11.6 | 23.7 | 13.5 | " |

* Broke in ext. mark.

have made a speciality of high strength brasses are now producing an alloy containing about 4 percent of manganese which gives from sand castings:

| Tons per Square Inch | | |
|---|---|---|
| Elastic Limit | Tensile | Elongation on 2 inches |
| 22.0 | 42—46 | 15-20 percent |

The alloy is largely used for propeller blades, etc.

The special high tenacity brasses present a wide field of useful research, not only on the constitution of brasses with one or more added metals but on their mechanical and working qualities. Doubtless a large amount of information on this subject has been accumulated by manufacturers and others as the result of experience, but much of it is not at present or likely to be generally available.

## TREATMENT AND UTILIZATION OF SCRAP AND RESIDUES.

The enormous quantity of brass scrap which has accumulated as the result of the war has brought into prominence the question of the economic treatment and utilization of this class of material. Whilst a large proportion of the scrap from war material is of a more or less special nature, every brass foundry and every firm concerned in the manufacture of brass produces a certain quantity of heavy and light scrap turnings, swarf, etc., and by-products such as ashes and skimmings, all of which have to be dealt with, and the way in which it is handled is a fairly good index to the efficiency of the works.

Most firms utilize their own heavy and clean light scrap, a certain proportion being added to each melting charge, and some foundries use certain of their own by-products. The majority of firms, however, find it is more economical to sell all by-products to a scrap dealer or smelter. Whatever the nature and quantity of the scrap material may be it is now generally recognized that a rigid system of collection and classification is of fundamental importance in its economic treatment whether utilized in the foundry or works producing it or disposed of to outside dealers.

During recent years there has been considerable development in the treatment of scrap on more scientific principles and new appliances have been introduced to facilitate such treatment.

Amongst these may be mentioned: disintegrating machines for disintegrating bulky turnings or swarf; magnetting machines for removal of iron; briquetting machines for compressing turnings or swarf; annealing furnaces for softening "springy" brass scrap; bundling or bailing presses for compressing sheet scrap; gas-fired furnaces for sweating tin and solder off light scrap; hydraulic presses for compressing or collapsing cartridge and shell cases.

Ashes, sweepings and other by-products are usually crushed in a ball mill or similar appliance, the crushed material classified, and the metallic portion separated from the waste by passing over a concentrating table of the Wilfley type. Old crucibles are crushed and the larger pieces of metal picked out by hand or by screening, whilst the remainder of the material is put through the concentrator and the fine metallic portions collected and dried and then sent to the metal store for further treatment and analysis.

The question of dealing with brass scrap, to get it into a suitable form for melting has received considerable attention within recent years. A method which was developed during the war period and has been successful consists in mixing swarf with a certain proportion of fluxing material, and compressing into briquettes, ready for melting. A number of specially designed machines have been introduced to compress the material into a compact form ready for charging into the crucible. Powerful bundling or baling presses are in use where large quantities of bulky scrap sheet brass have to be dealt with. These machines, which are usually hydraulically operated, press the material into bundles or bales of an average size of about 30 by 18 by 6 inches, which are subsequently melted in small reverberatory furnaces.

Very small or fine material is frequently charged into metal cases, such as cartridge or shell cases, and the whole subsequently compressed in a suitable press. This procedure greatly facilitates the melting of fine material and considerably reduces the melting losses.

With regard to heavy scrap which is usually returned direct to the foundry for remelting, experience during the war has shown that, where careful selection has been exercised, charges made up entirely of scrap have given castings and ingots equal in quality, and in some cases of superior quality, to that made from virgin

metal either alone or with the addition of small percentages of scrap. This experience has modified the generally accepted conclusion prevalent before the war that not more than about thirty percent of scrap should be added to any charge. Whilst much necessarily depends on the class of heavy scrap available, and the nature of the work for which the remelted metal is required, there appears to be little doubt that a few carefully conducted experiments made under suitable works conditions with the material available would prove that in many cases a much larger percentage of scrap might be employed than at present with economic advantage.

## PROVISION FOR RESEARCH.

Although research has been active during the past decade in dealing with the internal structure of the brasses and their behavior under mechanical and heat treatment, and much knowledge of practical value has been gained, it is generally agreed that there is still urgent need for more intensive research in the future interests of the brass industry. This urgency facilitated the recent formation of the British Non-Ferrous Metals Research Association, which was incorporated in January, 1920, and has for its object the prosecution of scientific and industrial research relative to the production, treatment and uses of non-ferrous metals generally. At the same time it endeavors to disseminate exisiting knowledge amongst manufacturers by means of a bureau of information and the periodic publication of a bulletin.

The Association seeks to coordinate and to cooperate in all researches being conducted on non-ferrous metals and alloys, and to initiate special investigation into problems that are of fundamental importance to the various industries concerned.

With regrad to the brass industry the Association has already conducted researches relative to the casting of brass and its properties and reports have been issued to members. Further research on the causes of red stains produced in the manufacture of sheet brass and other subjects is now in progress. Manufacturers are encouraged to bring their problems before the Association and to suggest researches that will be of value to the industry. These after the consideration and sanction of the

council in conjunction with the special research committees are taken in hand as far as the available funds of the association permit. For the immediate future the most pressing subjects awaiting more exact knowledge appear to be those connected with the economic melting and casting of brass and its mechanical and heat treatment during the numerous processes of manufacture.

In the brass foundry a good deal of information is really necessary which can only be obtained from systematic practical research, which has not yet been adequately done. Amongst the factors of importance in the melting and casting of brass ingots may be mentioned, the design of the furnaces, particularly adequacy and constancy of pull of the flue; laboratory supervision of quality of fuel, particularly in coke-fired furnaces; adequate protection of the metal during melting to prevent oxidation and ingress of gases; rate and method of pouring; shape and thickness of mould, its position and temperature during casting.

At the present time there is little exact knowledge available as to the correct casting temperature, and the best conditions of casting for the various qualities of brasses in use for industrial purposes. As previously pointed out electrical melting offers great possibilities, and the conduct of carefully planned investigations from the point of view of general foundry conditions and requirements would be of extreme value to the industry. The exact conditions that govern the economic rolling, stamping and hot-pressing of different qualities of brass also require further investigation. New uses for the industrial brasses now in general use are urgently needed and research might well be devoted to an attempt to solve this problem which is so necessary to the future welfare of this important national industry.

Reference has already been made to the increasing attention that is being given to the so-called high tenacity brasses and the need for further research in this direction. Engineers are urgently needing brasses that will withstand service at comparatively high temperatures and under high pressure, and there is a promising field for research in this important branch of the brass industry. Considerable attention has been given in recent years to the production of non-ferrous acid-resisting alloys, and

in this connection there appears to be scope for further research work on the addition to brasses of other metals such as titanium and the less known metals, with a view to attaining the object in view.

Problems await solution in connection with the extrusion of brass, as for example the prevention of the "coring" which frequently takes place in bars manufactured by this process. More exact and scientific information is required on the question of soldering and brazing and the composition of the alloys used. Stronger solders are required to meet the more exacting demands of modern engineering practice.

Such in brief are in the author's opinion some of the more urgent problems that await solution in the brass industry. Whilst it is true that a large amount of data relative to these various problems has been accumulated in recent years much of this is of little value to the manufacturer owing to the lack of essential details and the unscientific manner in which the investigations have in many cases been carried out. If they had been carried out with due regard to the objects for which the metals and alloys are to be applied in industry the results would probably have been of much greater value. It is now fully recognized that research, the object of which is the acquisition of new knowledge, is a fundamental necessity to progress, consequently the future development of the brass industry will largely be dependent on the extent to which it encourages research and undertakes investigation on its own behalf.

## ORGANIZATION AND COOPERATION.

One of the great lessons that has been learned during the war is the magnificent result of organization and improved methods of intensive manufacture. This lesson has not been lost on manufacturers in the brass industry and during the reconstruction period they have considered what is necessary to be done to make their production more efficient. It has been realized that the solution to progress in industry consists in improved methods of manufacture, improved organization, standardizing processes and reducing the cost of output. There were indications of a desire amongst firms in the same trade to organize, each firm specializing in parts, and progress in this direction

has been made. The question of cheapening production in the brass industry by a system of amalgamation, standardization and concentration was brought prominently before manufacturers three years ago by the publication of a pamphlet on a "Scheme of Syndication for the Brass Industry," by Howard F. Smith, of Birmingham.

It is generally agreed that in the past and even at the present time a great source of wasted energy is that so many manufacturers are engaged in a miscellaneous trade, with no economic standards. Ten firms may each be manufacturing ten different types of articles at a loss, whereas, if each concentrated their attention on one type, the loss would be converted into a profit. That an economic limit of production should be established in each case is obviously a necessity, but the economic unit is not necessarily large. For example, it was proved during the war that many small firms were capable of manufacturing shells at least as cheaply as the largest organizations. These factors have been duly considered in the light of modern industrial requirements with the result that there has been a number of combinations of small groups of firms interested in particular sections of the brass industry. Such combinations are greatly to the interests of the industry as they abolish competition between the firms themselves and enable them to compete successfully in the world's markets. Combination in the brass industry presents some difficulty however, owing to the diverse nature of its products. Firms so diverse for example, as manufacturers of bedsteads, fenders and general household metal work, on the one hand, and brass tube makers and wire-drawers on the other, are illustrative of the great diversity of trade in Birmingham.

Another important factor bearing on the question of economical standards is the sad neglect of standardization of types, and the unnecessary variations that have been allowed to intrude themselves, merely to satisfy individual tastes, and because it has been nobody's business to see that they are reduced to a minimum. This question of standardization is one of considerable moment to the future of the brass industry, and it is gratifying to know that it has now been taken in hand by the British Engineering Standards Committee, which hopes in due course

to issue specifications to cover all the varied uses to which the brasses are applied in industry. When these are issued they will no doubt lead to the discontinuance of a number of alloys now in use and to greater cooperative effort in the efficient and economic production of the accepted standard alloys, the value of which was emphasized during the war period.

From what has been stated in the foregoing pages it will be evident that considerable progress has been made in the British brass industry during the past decade and that manufacturers as a whole are awake to the fact that the industry has now entered upon a new era of its history. Consequently they are taking steps to effect the reconstruction that is so vital a necessity if the industry is to maintain that position in the world's markets which the high quality of its products has secured for it in the past.

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## DISCUSSION.

ACHESON SMITH[1]: A few weeks ago, in discussing some matters pertaining to the Society with Dr. J. A. Mathews, he suggested that it might be helpful if a paper could be written on the comparative practice in Great Britain and the United States, both in steel and in non-ferrous electric furnace work, if it would be possible to get the data for such a paper. It would probably be illuminating to the industries in both countries.

[1] Vice Pres. and General Manager, Acheson Graphite Co., Niagara Falls, N. Y.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# RESISTANCE TYPE ELECTRIC FURNACE IN THE MELTING OF BRASS AND OTHER NON-FERROUS METALS.[1]

By T. F. Baily[2].

## INTRODUCTION.

In considering an electric furnace for melting non-ferrous metals, the various features to be considered in making the installation should be as follows:

(1) Quality of metal produced as a result of melting in the furnace.
(2) Simplicity of construction as it influences reliability for continuous operation and ease with which furnace can be handled, resulting in the minimum of attention.
(3) Current consumption per ton of metal of required quality.
(4) Electrical load factor of the furnace with reference to the cost of current per kilowatt hour.
(5) Power factor of the furnace, as it may influence the electricity rate earned.
(6) Labor for controlling the furnace itself, exclusive of metal handling.
(7) Labor required for charging and pouring the furnace.
(8) Adaptability of the furnace to the various alloys that it may be required to melt, without change in construction.
(9) Adaptability of the furnace to melt different classes of raw material.
(10) Renewals, repairs, and upkeep, including linings for the furnace itself, hearth linings, resistor material, etc., as well as the labor required for putting in the same and the time furnace is shut down for such renewals and repairs.
(11) Total cost per ton of cast material meeting specifications.

[1] Manuscript received August 29, 1921.
[2] Vice President, The Electric Furnace Co., Alliance, O.

(1) In dealing with the first requirement, namely, the quality of metal produced, the resistance type furnace has a distinct advantage in the fact that it can be completely and tightly closed, and the reducing atmosphere of the furnace, which is always present when the furnace is closed, as a result of the carbon resistor material being in free contact with the furnace chamber, can be maintained, which is of great advantage over a furnace where an oxidizing atmosphere is present. Also, the fact that the furnace is a true open hearth, so that it can readily be skimmed, if the charge is dirty, or if any fluxing operations are required, is an additional advantage in readily producing the highest grade metal. It has frequently been mentioned that the resistance type furnace, since it does not rock and does not agitate the metal, or since the metal is not agitated by being a part of the heating element itself, cannot get a thorough mix of the charge. However, it must be admitted for any alloy, if the proper temperature is present, that all the components will quickly become thoroughly diffused in the bath. In the case of mixtures containing lead, this metal—since it is not an alloy, but only a mechanical mixture—must be stirred in any furnace.

(2) The simplicity of construction, as it influences the ease with which the furnace can be manipulated and reliable operation obtained, is of paramount importance in its relation to the cost of operation. For it is obvious that if a furnace is difficult to handle, and requires highly skilled and constant attention in order to produce good metal, there is more likelihood that a larger percent of off-grade castings will be produced; or, at best, the cost of producing good castings will be materially increased. Here again the true open hearth of the resistance type furnace is of marked advantage, since it has no obstructions—either electrical or mechanical—and free access is had, so that the charging of the metal, together with skimming or other mechanical operations, which may be required with some classes of metal, can readily and easily be done. The fact that the heating element is located at a considerable distance from the hearth, and where it cannot readily interfere with these operations, is another advantage; as there is not so much likelihood of damaging these parts, as is the case in other types of electric furnaces, where the

heating units—whether tubes or electrodes—are so placed that they may be subjected to mechanical damage in charging, or where renewal of the same requires interference with the hearth.

Again, the simplicity of construction of the resistance type furnace has an advantage with regard to repairs, since if the hearth needs repairs, such as patching or renewal, this hearth, being in no way connected with any obstruction or special electrical connection, may readily be repaired. In the same way, if the resistor elements need replacing, this can readily be done by raising the roof, where free access to these parts is obtained, and this work carried on without interference to the hearth. Further, for these repairs there is not required the skill as is the case for such operations in other furnaces; but only such as may be needed in the average fuel fired furnace. In addition to this, the furnace of the resistance type is not subject to sudden failure of any of its parts, as indications are usually given for a long period beforehand when such renewals are required, and a convenient time can be selected for the needed repairs.

(3) As to the current consumption per ton of metal, the resistance type furnace, owing to its relatively large exposed wall surface in proportion to its melting capacity, as compared with other types of melting furnaces, has a higher current consumption per ton of melt than either arc or induction furnaces, and may run, under general operating conditions, substantially 100 kilowatt hours per ton more than an induction furnace, and, perhaps 50 kilowatt hours more per ton than the arc furnace.

(4 and 5) However, taking into consideration the electrical load factor of the resistance type furnace, which is substantially unity, since the power need never be turned off during charging and pouring, but held at constant wattage, the heat during this time being stored in the walls without overheating either the metal or the furnace itself and readily given out to the cold charge immediately after pouring and re-charging, in the average central station figures will frequently show a lower cost for electricity per ton of metal than any other type of furnace, excepting the induction type.

(6) As to the labor for controlling the furnace itself, the resistance type furnace is undoubtedly the simplest melting unit;

since all that is required is to set the control switch at the required electrical input for a given capacity, after which there is substantially no variation in the input; and, once the power is turned on and the furnace charged and poured at a desired operating rate, no change in this switch is required for hours at a time. This is a great advantage over melting units that require constant and almost instantaneous adjustment in order to hold the power input within reasonable limits; and thus the electrical control of the resistance type furnace is almost a negligible item, and may be likened to the simplicity of operating an incandescent lamp circuit.

(7) As to the labor required for charging and pouring the metal, together with any rabbling that may be required for handling dirty metal; again the true open hearth furnace has a marked advantage, since all parts of the bath may be readily seen and stirred, or rabbled; and, since the charging is done through a relatively large door, large pieces of heavy billets, or other unwieldy raw material, can readily be handled with little danger of abrasion of the hearth; while in other types of furnaces, such heavy material requires the most careful handling to prevent damage to the electrical equipment. The resistance furnace of the nose tilting type is especially adapted for rolling mill work, particularly when equipped with a casting table, reducing the labor in pouring to a minimum, since one man can take care of both the tilting of the furnace for pouring and the shrinking of the molds.

(8) When considering the adaptability of the resistance type furnace to various metals, it has a distinct advantage over types of furnaces that use a part of the charge for developing heat in the electric circuit, since the heating element is entirely separate and apart from the charge. And again the true open hearth type lends itself more readily to constructing a hearth lining of maximum strength and resistance to impregnation; and a brass or copper alloy may be handled on a standard hearth without other operation than giving such hearth a wash heat to clear it from contamination by any previous alloy.

(9) In the melting of different classes of raw material, the fact that the resistance type furnace has a large hearth area and

the furnace a larger cubical content than any other furnace, when measured with reference to touching any electrical part of the furnace, so that in handling very light material fewer charges are required per given hearth capacity. And again, since the hearth is free from any delicate electrical connections, as is required in some types of furnaces, less care is necessary in charging heavy and rought material with reference to danger of breaking important electrical parts.

(10) As to renewals and repairs, as has been previously mentioned, these are more readily accomplished and with less skill than in any other type of furnace made—the hearth lining being as simple to put in as in an ordinary reverberatory furnace. The electrodes, since they are completely covered with carbon at all times, last for months at a time without attention and adjustment, and are a negligible item in the cost of furnace operation. The resistor material, which it is necessary to renew on an average of once in two months, is readily replaced by raising the roof, which is supported on three screws operated from a common gear wheel; and this operation can be accomplished in a few minutes, usually being done at the end of the week. The lining of the furnace proper consists of standard circular brick, which may be laid by any brick repairman, and the carborundum troughs and the piers which support them require no special skill, since they are formed to shape and are readily set in place and the resistor material shoveled in. The fact that the resistance type furnace is not subject to shut-downs without warning, as happens with other types of furnaces, is a distinct advantage, and a convenient time may be selected for substantially any repairs that may be required. It has sometimes been mentioned that one of the defects of the resistance type furnace is that it is exceptionally hard on refractories, and that the roof particularly requires frequent renewal; but in this instance, almost without exception, the destruction of the roof or refractories of the furnace has been the result of leaving the power on the furnace at full capacity for many hours without any charge on the hearth, and hence such repairs are the result of extreme carelessness and should not properly be charged against the furnace.

(11) In summarizing the various advantages and disadvantages of the resistance type furnace as compared with other types, it is to be noted that, based on current consumption alone per ton of metal melted, the resistance type furnace does actually take more kilowatt hours per ton than any other type; but it is also to be noted that it earns, in most cases, as compared with other types, a better power rate, and that if the cost of electricity per ton of metal is at the usual rate which obtains from central stations for such service, then the actual cost per ton of metal melted for electricity is, in most cases, less when the resistance type furnace is used than when the arc type furnace is used; then, when taking into consideration rates where a penalty is made by the central station due to low power factor, the advantage of the induction type furnace as to lower current consumption per ton of metal melted is, to some extent, offset. Then, the labor for controlling the resistance type furnace is materially less than the arc type; and, due to its larger capacity per unit, is also lower in cost of furnace operation than the induction type. Again, as to the labor required for handling the metal in the furnace, the larger capacity of the resistance type furnace, as compared with the induction furnace, is an advantage; and, due to its simplicity of operation, the resistance type furnace requires a smaller crew to handle than is the case with the arc type furnace. Due to its ability to handle various mixtures, it has a distinct advantage over the induction type furnace, which must be built distinctly for one mixture, and cannot, from an electrical standpoint, be used for any other metal, without replacing the entire bottom of the furnace. As compared with the arc type furnace, the hearth arrangement is such as to make it possible to build a much more substantial hearth lining than in furnaces of the arc type; and the same simplicity of construction gives a similar advantage with reference to the melting of various classes of raw material of any analysis.

So that, when taking into consideration the total cost per ton of merchantable castings or bars produced, and adaptability over a wide range of alloys, such as must be met with in any mill or

foundry, the resistance type furnaces comes more nearly filling all the requirements than any other type of electric furnace for melting now made.

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## DISCUSSION.

H. M. St. John[1]: There are several statements in this paper to which exception might be taken, but I cannot conceivably discuss them all without taking more time than I should. For one thing, I believe that the author has, in certain instances, claimed as special advantages for the resistance type of furnace, advantages which, in reality, are common to all successful brass-melting electric furnaces. However, I wish particularly to discuss the question of power cost. As most of you know, the price of central station power is based on two factors, the maximum demand and the energy consumption.

Mr. Baily has generously granted that the type of furnace he is discussing uses more kilowatt hours per ton than do other types, but he argues that, because of the peculiar construction of the furnace, a kilowatt hour used in his furnace costs less than a kilowatt hour used in some other furnace, to such an extent that the net cost of electric energy per ton with the resistance furnace is actually less than with other furnaces which use many less kilowatt hours per ton. This conclusion is not even partially correct.

In any type of electric furnace the maximum demand is greater than the average use of electric energy, the difference being least, probably, in the induction furnace. In the type of arc furnace with which I am most familiar, the maximum demand is about 20 percent above the average power consumption. I am familiar with several plants where the resistance furnace is in use, and have seen numerous charts showing the demand of the furnace in different stages of its operation. I am certain that all of the charts I have seen show a maximum demand at least 20 percent above the average use of energy.

[1] Service Manager, The Detroit Electric Furnace Co., Detroit, Mich.

In this connection it must be remembered that the instantaneous demand of the furnace, no matter what the type, has virtually no effect on the maximum demand, since the maximum demand rates of nearly all central stations are based on an average demand over a fixed period of time, usually not less than a half hour, and in some cases over much longer periods. It is obvious that, under these circumstances, an instantaneous demand—lasting perhaps three or four seconds—even though it may conceivably be 50 per-cent greater than the average demand, has little or no effect on the demand rate. I do not know of a case where the electrical characteristics of any furnace could possibly reduce the power rate sufficiently to counterbalance a 100 kw. hr. per ton difference in energy consumption, or even 5 percent of 100 kw. hr. This point is an exceedingly important one and has been much misunderstood.

H. W. GILLETT[2]: The laws of heat flow seem to be suspended for the special benefit of the resistance type furnace. On page 373, paragraphs 4 and 5, we read that the power is not turned off during pouring, but that the heat is stored in the walls without overheating the charge. This can only be true when the furnace is operated in a manner impossible in practice. It could be true if the last end of the heat is run so slowly that the resistor and roof are not at a decidedly higher temperature than the charge. But, unless the resistor and the roof are much hotter, the rate of heating will be slow, the production low, and melting costs excessively high.

As a matter of fact, to get any sort of output or efficiency from the resistance type, it ought to be run at as high a power input as the resistor trough will stand, and its operators generally aim to run it so. In that case there is stored heat in the resistor and roof at temperatures much above the desired pouring temperature, and if the charge is not poured when the desired temperature has been reached, the charge will overheat unless the power input is cut off, or reduced to the point where it equals the heat leakage from the furnace, or unless more cold charge is added. In fact, the temperature of the charge will continue to rise from the stored heat even if the power is cut off, in usual practice.

The combination of operation at unity load factor and constant

[2] U. S. Bureau of Mines, Ithaca, N. Y.

temperature during pouring is an impossible one unless pouring is instantaneous.

The final conclusion, page 377, is certainly open to question as to the foundry, and as to the mill, the preponderance of other types in rolling mills indicates that a small proportion of rolling mills agree with the author of the paper.

H. M. St. John: On page 373, paragraph 3, the statement is made that the resistance type of furnace may use, under common operating conditions, substantially 100 kw. hr. per ton more than the induction furnace, 50 kw. hr. per ton more than the arc furnace. Exception must be taken to this differential between induction and arc furnaces. As a matter of fact, in rolling mills—the only type of plant where arc and induction furnaces can be directly compared—the size of arc furnace ordinarily used in such mills shows an energy consumption quite as low as shown by the induction furnace, in certain instances even lower.

J. A. Seede[3]: One of the points brought out by Mr. Baily, that is in regard to labor of controlling the furnace, may convey an erroneous impression. I feel sure that the labor required to manipulate the control switches for the resistance furnace is undoubtedly as great as the labor required to adjust the automatic control of any arc furnace, and it is well known that there are one or more thoroughly reliable automatic controls which meet these conditions.

F. B. Steele[4]: I would like to ask what is the maximum heat consumption required per ton, brass furnace, rating the furnace as one ton.

T. F. Baily: In continuous melting?

F. B. Steele: The maximum, whatever your maximum is; kilowatt consumption.

T. F. Baily: About 350 in one-ton per hour capacity. In the best rolling mill practice, making cakes for condenser tubes, based on continuous operation, including the heating up over Sunday, the minimum current consumption per ton of cakes poured has been as low as 260 kw. hr. per ton.

[3] Electrical Engineer, General Electric Co., Schenectady, N. Y.

[4] Ass. General Manager, Utica Gas and Electric Co., Utica, N. Y.

COLIN G. FINK[5]: What is the maximum melting point of alloy or metal that can be successfully run in the Baily furnaces today, and the maximum temperatures?

T. F. BAILY: Well, I think the highest temperature material that we run commercially is copper; the highest melting metal we have actually run in one of these furnaces in our own laboratory over a period of several days was 0.05 carbon steel, with the highest temperature above 3360° F., about 1850° C. That was of an experimental nature and lasted only three days, but the furnace was still in operation at that time.

J. W. RICHARDS[6]: Have you noted any substantial difference in the amount of power required to melt the metal depending on whether it was white, like aluminum, or red like copper, or black like steel, in its power of quickness of absorbing heat?

T. F. BAILY: Aluminum is difficult to melt, slow to take the heat, and requires a greater temperature differential between furnace and metal. On the other metals we have never noticed any particular difference.

F. A. LIDBURY[7]: Is the difference in the specific and latent heat, or is it a marked difference of color, as I understood Dr. Richards to suggest?

J. W. RICHARDS: Difference in the rate of heat absorption.

F. A. LIDBURY: Which is it, as a matter of fact?

J. W. RICHARDS: It depends on the color, essentially. Black metals will absorb heat much more rapidly than the white ones. You put a piece of black metal in the furnace and see how much quicker it will heat up than a piece of white metal, because of its absorbing power.

H. M. ST. JOHN: I have had some experience in melting copper, red brass, yellow brass, aluminum, iron and steel under such conditions that it was possible to determine the approximate thermal efficiency of the furnace, and I have never found that there was an appreciable variation in the thermal efficiency of the fur-

[5] Consulting Electrometallurgist, New York City.
[6] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.
[7] Works Manager, Oldbury Electro-Chem. Co., Niagara Falls, N. Y.

nace when melting these metals of differing color, other than would naturally be expected from the difference in pouring temperature required for each. Of course, the higher the temperature to which the metal must be heated, the lower the efficiency of the furnace. I doubt if the difference of color exercises a measurable influence on thermal efficiency, using the term measurable as applied to a commercial installation, where measurements are taken with industrial rather than laboratory instruments.

H. W. GILLETT: While materials heated in the open absorb varying amounts of heat, and emit different amounts of light, due to their reflecting power and consequent deviation from a "black body," if they are inside a uniformly heated enclosure, they emit black body radiation.

Platinum is far from a black body in the open, but inside a uniformly heated carbon tube, the platinum will be invisible. A closed furnace closely approximates a "black body enclosure," and since all materials in such an enclosure emit black body radiation, it is probable that their ability to take up heat inside the furnace is not much affected by their deviation from perfect absorptive power in the open.

J. W. RICHARDS: I agree entirely with Dr. Gillett.

J. A. SEEDE: Some experiments made by Mr. Collins have a direct bearing on this subject, being approximately as follows:

One inch cubes of aluminum and copper were placed separately in a small furnace and each heated under similar conditions, and in this experiment it was found that the aluminum cube absorbed heat about 70 percent as fast as the copper cube.

H. W. GILLETT (*Communicated*): The radiation from an enclosure, all parts of which are at the same temperature, is black body radiation, no matter what the enclosure is made of.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# COMPARISON OF ELECTRIC FURNACE PRACTICE WITH FUEL-FIRED FURNACE PRACTICE.[1]

By N. K. B. Patch.[2]

Abstract.

In comparing the electric with the fuel fired furnace, the important considerations are, cost of electrical energy, or fuel, and efficiency of operation. The author's experiences are that the cost of metal melted, the melting losses, and the solution of gases in metal, are substantially the same in the electric furnace and the fuel fired furnace, provided intelligent operation is pursued.

[A. D. S.]

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Our experience with electric furnace melting began with the installation of one Baily electric furnace early in 1916; later, a second was added and was followed by a third. The first Baily was used in melting our Lumen alloy—a zinc base alloy of relatively low melting point. It gave very satisfactory results from the first, and the other two have also worked out very well on alloys with higher melting point, such as phosphor bronze and manganese bronze. These furnaces are in daily operation.

In 1920 we added a Detroit rocking electric furnace with automatic electrode control. Our experience indicates that each electric furnace has its particular adaptability; that is, a Baily is to be preferred to the arc type of furnace, for the production of certain types of alloys, even though it consumes a larger wattage than the other types. It is also advantageous to use the arc type of furnace for other types of alloys, both because of the larger production as well as the lower cost.

It is entirely probable that experience will indicate the pre-

[1] Manuscript received, September 2, 1921.

[2] Works Manager, Lumen Bearing Co., Buffalo, N. Y.

ferred application of each of the types of electric furnaces, the resistance type having a certain definite field, the arc type another and the induction type still a third field within which its success is most marked.

In comparing the cost of operating electric furnaces with fuel fired furnaces, of either the hearth type or the crucible type, many things must be borne in mind. The location of the plant with reference to a source of power is, of course, paramount. Obviously, cheap electric power will give the electric furnace a decided advantage. Located as we are in Buffalo, this first requirement is well provided for.

Next in order, it seems to me, is the efficiency of the combustion of the fuel in a fuel fired furnace. Where fuel is grossly wasted, electric furnaces will indicate an advantage, which is entirely unwarranted. Our oil consumption in our fuel fired furnaces is, we believe, as low as is the practice in any of the plants, so that in comparing our costs, both the electric and fuel fired furnaces are easily worthy of normal comparison.

Next in importance in considering costs is the relative cost of labor on the two types of furnaces. Neither type of furnace is fool-proof, and it is our experience that the greater capacity the furnace may have per hour, the greater intelligence is necessary in its operation. This is true in both types of furnaces.

In considering the advantages that each may have over the other, the outstanding advantage of the electric furnace is its cleanliness, and comfortable operating conditions. On the other hand, a fuel fired furnace still has a decided advantage over the electric furnace in the consideration of first cost. Our experience has indicated that after considering all items which make up the cost, such as fuel consumption, refractories, repairs, maintenance, wages to operators, etc., under the conditions under which we operate at low fuel cost, and low current cost, the cost per 100 pounds of metal melted is practically the same in either type of furnace.

The claims of the electric furnace manufacturers for marked saving in melting loss are somewhat exaggerated. It is true that certain types of alloys may be melted in an electric furnace with a reduction in this loss, as against melting the same alloy in inefficiently operated fuel fired furnaces. Properly operated fuel fired

furnaces, however, will compare favorably on this score with electric furnaces.

The sensitiveness of non-ferrous alloys to the solubility of gases during melting is such that the atmosphere of any furnace must be carefully considered. The electric furnace more or less improperly handled is just as liable to cause trouble as the fuel fired furnace is, as the combustion of the electrodes, or resistance materials, is an ever present source of CO gas, which is readily soluble.

We, therefore, believe that any consideration of the relative advantages of the electric furnace as compared with the fuel fired furnace, both as to the standpoint of cost and quality of metal produced, resolves itself to the consideration of two prime factors—one the cost of the current or fuel, and the other the intelligence of the operator. Given low fuel cost and low current cost, and satisfactory intelligence in operation in both cases, the one is no cheaper than the other, but the quality of the metal in some of the more sensitive alloys is more reliable in melting in electric furnaces. The reduction in the cost of rejected castings indicates an advantage in favor of the electric furnace, in our opinion, enough to compensate, in some degree, for the difference in the first cost of the equipment.

Alloys that are sensitive to hydrogen gas, superheated nitrogen and carbon should show marked improvement when melted in electric furnaces under intelligent control.

We have had no experience with the operation of induction electric furnaces, our remarks referring to other types. It is entirely probable that an induction type of furnace, through its entire absence of the superheated gas problem, offers a solution of the problem above mentioned, of the sensitiveness of the alloys to the solubility of many of the gases of combustion. There are, no doubt, inherent weaknesses in induction furnaces, which counterbalance to some extent this advantage.

It is difficult for us to give actual cost figures in regard to the above comparison, as we are manufacturers of brass castings from an extremely varied line of patterns, and a large number of different alloys. It is obvious that a jobbing brass foundry may be called upon to make castings from almost any

alloy, and to almost any type of pattern. Such a condition must necessarily make cost comparisons of more or less doubtful value, since there are so many variables in the conditions which cannot be standardized, in order to make the comparison of any real value.

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## DISCUSSION.

E. L. CROSBY[1]: I am glad to see a paper on an electric furnace for brass by a man who does not have an electric furnace for sale.

H. W. GILLETT[2]: Mr. Patch says that the induction furnace "offers a solution of the superheated gas problem, of the sensitiveness of the alloys to the solubility of many of the gases of combustion." This is too sweeping. The induction furnace, unless charcoal is put on to prevent or mitigate it, will have an atmosphere high in oxygen over the metal, while in the arc and resistance types, oxygen is mainly combined as CO. In many cases a superheated atmosphere with low oxygen or zero oxygen would be better than a cooler atmosphere high in oxygen. That feature of the induction furnace might be either an advantage or a drawback, depending on what was being melted.

C. B. GIBSON[3]: Mr. Patch has made the statement that the cost of melting brass in the electric furnace is substantially the same as in the fuel fired. He then points out the difficulties in arriving at any reliable comparative cost. In this connection, I have noticed that in several of the papers presented this morning, reference is made to the cost of melting and relative saving of one process over another, but the costs and other data are not fully qualified. I think we are likely to draw incorrect conclusions, unless these costs are fully qualified. Our experience has been that it is extremely difficult to obtain reliable comparative costs for electric melting over the older known methods.

This is particularly true now when most companies are operating only a few days a week or a few hours a day. In our own

[1] Vice Pres. and General Manager, Detroit Electric Furnace Co., Detroit, Mich.

[2] U. S. Bureau of Mines, Morse Hall, Ithaca, N. Y.

[3] Manager, Metal Mining and Chemical Section, Ind. Dept., Westinghouse Electric & Mfg., Co., E. Pittsburgh, Pa.

brass foundry, where we are working on a considerably reduced schedule, it so happens it is somewhat less expensive to operate the fuel-fired instead of the electric furnace. However, under anywhere near normal operation, a condition for which industry at present is hoping, and considering all other factors, there is a material saving in the electric process. The amount of this saving varies, depending upon local conditions of the particular installation. I think, therefore, in our discussions, the relative costs between the electric and fuel-fired furnace should include as complete qualifying data as possible.

G. K. ELLIOTT[4]: I should like to ask Mr. Gibson how much the fuel cost him; is it oil or gas?

C. B. GIBSON: Both oil and gas. We pay the prevailing market price for oil, which has varied considerably during the past year.

G. K. ELLIOTT: Natural gas?

C. B. GIBSON: Yes.

G. K. ELLIOTT: I would also like to ask how many users of brass electric furnaces there are in this crowd today?

ACHESON SMITH[5]: Does anybody wish to volunteer or admit that he is an operator? I do not see any volunteers.

COLIN G. FINK[6]: May I just say a word in reply to some of these remarks about the papers on electric furnaces submitted to us by the manufacturer of electric furnaces? There is always a development in the line of papers presented before the Electrochemical Society. When a new tool like the electric-brass furnace first appeared, there were no users; we had to go to the manufacturers. They were the only ones who knew anything about it. The little they knew we asked them to give, and what they did not know the first year we asked them to give us the next year. The first paper on the Söderberg electrode was presented by the manufacturer. The second paper on the Söderberg electrode was presented by a user of the Söderberg electrode. Now I do not know what the third paper will be, but Dr. Richards gave you some idea yesterday as to the extent of the installation of the

[4] Chief Chemist and Metallurgist, The Lunkenheimer Co., Cincinnati, O.
[5] Vice Pres. and General Manager, Acheson Graphite Co., Niagara Falls, N. Y.
[6] Consulting Electrometallurgist, New York City.

Söderberg electrode. That is a natural sequence. Mr. Crosby's remarks are timely, and we all hope that the next time we get together and talk brass, we will have papers presented by the rolling mill people.

J. W. Richards:[7] Last year I was in the plant of the Lumen Bearing Company, and was much interested to see that the Baily furnaces there were the ordinary dark brown rust color. They were just installing a new Detroit arc furnace, which was painted white with aluminium paint. I called their attention to the difference, and complimented the man who painted his furnace white. My experience with it, quantitatively, is that it makes about ten percent difference in the power required in the furnace. Now, while power requirement is not the whole thing, it should be economized by such a simple means.

N. K. B. Patch (*Communicated*): Dr. H. W. Gillett states that I say "The induction furnace offers a solution of the problem in connection with the absorption of gases, when superheated;" whereas, I was careful to note in my paper that "We have had no experience with the operation of induction electric furnaces, our remarks referring to other types. It is entirely probable that an induction type of furnace, through its entire absence of the superheated gas problem, offers a solution of the problem above mentioned, of the sensitiveness of the alloys to the solubility of many of the gases of combustion." This explicitly says that the fact must be proven and can only be answered by those who have had experience with the induction furnace.

In reply to Mr. Gibson's remarks, as to comparative cost data, he is entirely correct in stating that "comparative cost figures should be qualified as much as possible." Therefore, when furnace manufacturers make claims for low cost operation or compare the cost of their furnace, from any standpoint, with any other type of furnace, such cost figures, or comparisons, should be properly qualified.

[7] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# ELECTRIC SILVER MELTING.[1]

By H. A. DeFries.[2]


## Abstract.

Silver melting in the electric furnace eliminates high crucible cost and the necessity of an experienced melter, which are essential to gas or oil fired crucible practice. Distinction is made between pouring temperatures of bar silver (1038 to 1093° C.) and of rolling mill and casting silver (1293 to 1304° C.), when casting horizontal moulds. To produce a ductile silver temperature control, a reducing atmosphere and a quiet molten bath are essential. A more ductile and tougher silver results upon introduction of an iron block into the bath. An electric silver melting equipment is described and cost of casting rolling mill silver.

[A. D. S.]


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Silver is recovered mainly from auriferous silver bullion called doré, by electrolytic separation. It is then melted and fined in a furnace to be at least 997 pure and cast into ingots, in which form it is commercially known as bar silver.

Silver melts at 962° C. (1764° F.). It volatizes at high temperature, giving off a green vapor. In the molten state it has the property of absorbing 22 times its volume of oxygen, which is given off on cooling, causing the so-called "spitting" of silver. This, however, happens only with the pure metal. Small quantities of copper or zinc entirely prevent it as does also an inert cover. Arsenic, antimony, bismuth, tin and lead render silver brittle.

Besides the bar silver, the silver most commonly used is sterling silver, which is of 925 fineness.

[1] Manuscript received August 5, 1921.

[2] Consulting Engineer, New York City.

Bar and sterling silver have been melted mainly in crucibles, either gas or oil fired, and charcoal is always used for a cover.

The danger with these methods of heating is that the silver becomes contaminated by the sulphur in the fuel. It is a well-known fact that in such operation a marked difference will appear in the metal when using oils of varying analysis and even a change in the barometric condition of the air will be immediately noticeable in the crucible.

The cost of crucible renewals is heavy and should a crucible break the silver, which runs into the pit and has to be dug out, cannot be used again without previous refining.

For these reasons it is obvious that the crucible melting of silver is expensive and only the most skilled melter is assured of reasonable success.

The electric furnace, on the other hand, being free from these objections, possesses, therefore, great advantages over the crucible. I will give herewith my experience in melting fine and sterling silver by the electric furnace method.

To begin with, we have to make a distinction between melting silver first into bars for subsequent remelting; second into skillets for rolling or into castings.

## I. BAR SILVER.

As stated, the melting point of silver is 962° C. (1764° F.) and a pouring temperature of about 1038 to 1093° C. (1900 to 2000°F.) has been found sufficient to cast silver into bars. This process is carried out as follows:

Silver is charged into a furnace preheated to about 1038°C. (1900°F.) and when molten it is covered with charcoal. The metal is gradually heated up to about 1205° C. (2200° F.) and poured at about 1093°C. (2000°F.). Before pouring, a test is taken by dipping a rod into the bath. The sample on the end of the rod should show no spots on the surface and have a pure silver white color. The metal is poured either directly into moulds, or into a pot or crucible. The latter should always be thoroughly preheated and covered with charcoal.

When filling the moulds, which should have been warmed and smoked, a small stick is held in contact with the surface of the silver to collect any floating slag or impurities. As soon as the

mould is full a small piece of paraffin is thrown on the metal By this method smooth bars are obtained, but they cannot be used for rolling.

An excellent example of this practice are the runs at the U. S. mint in Philadelphia, where over 3,000,000 lb. of silver dollars were remelted into bars in a 1000 lb. Rennerfelt electric furnace, with a metal loss of 1/100 of 1 percent or equal to 1 oz. in 10,000 oz. The power consumption for this work averaged 180 KWH per ton and the acid lining of this furnace outlasted the entire run.

### II. MELTING ROLLING MILL SILVER AND CASTING SILVER.

As previously stated, the pouring temperature for bar silver is about 1093° C. (2000° F.). If, one, however, would endeavor to pour silver at this temperature into rolling mill stock or into castings, the resulting materials would be so brittle as to be entirely worthless for subsequent working. Therefore, special methods have to be employed. These methods were recently worked out by the experiments the writer made at the plant of the Gorham Company. At this plant a specially designed electric furnace of 10,000 oz. capacity is in use and all runs and tests were made on an average of 4000 oz.

What is said in the following will refer to fine silver as well as sterling, as I have found little difference in the behavior of the two metals. In general the following points should be strictly observed:

*1.* The proper temperature at which rolling mill and casting silver should be poured is 1293 to 1304°C. (2360° to 2380°F.), when cast into horizontal or nearly horizontal moulds and 1204° C. (2200° F.) when cast into vertical moulds.

In practice horizontal moulds are set on an incline of 5°. If the metal is poured at a higher or lower temperature than the one given, brittle ingots will result and the closest temperature control is, therefore, essential.

*2.* Silver should be prevented from absorbing its customary amount of oxygen from the beginning of the melt.

As previously intimated, an inert cover or the addition of small quantities of copper or zinc prevent this absorption. Large amounts of charcoal are objectionable in most operations, as it

has to be removed before pouring. The use of copper and zinc is limited, as the silver must be kept within 1/1000 of the standard and even the smallest addition of copper and zinc will alter the assay standard more than is permissible.

We must, therefore, look for other means of overcoming these difficulties and same are easily found by taking advantage of the melting conditions in the electric furnace. Every electric furnace can be made fairly airtight, thus making its atmosphere independent of outside conditions. The electrode furnaces generally supply enough carbon from their electrodes to create a slightly reducing atmosphere and by adding small amounts of powdered charcoal they can be made more strongly reducing. We thus have a medium of producing the proper atmosphere without having to resort to large amounts of reducing agents.

Having obtained the proper atmosphere in the furnace the silver must remain quiet; never be disturbed by rocking or stirring, as this would immediately bring unprotected silver in contact with any entering gas and thus disturb the equilibrium of the charge.

Good ductile silver can be produced by this method and the maximum amount of powdered charcoal to be added will not exceed 1 lb. per 5000 oz. of silver.

It was the desire of the Gorham Co. to produce silver much more ductile and tougher than any produced so far in crucibles. We resorted to the old English practice of putting a block of iron in the bath. The results then obtained exceeded all expectations, as is evidenced by the tests given later. The correct performance of this iron block I have not as yet been able to solve. The English melters claim "it gives the silver the heat," and they are correct in this assumption, as it certainly acts as a stabilizer towards the heat in the silver. I believe, however, that it performs a more important function. It seems that not all the oxygen occlusion is eliminated by the proper furnace atmosphere or the addition of copper, but that some oxygen is retained in the metal. The iron probably absorbs these remaining traces of oxygen or enough of it to produce a metal of the correct pitch.

My attention was called to the fact, that most iron metallurgists are wary about admitting the occlusion and absorption of oxygen by iron at such low temperature.

That oxidation of the iron takes place is evidenced by the fact that the block becomes pitted after being used various times and gradually diminishes in volume. This matter, therefore, warrants closer investigation.

*3.* The next important item is the handling of the metal from the furnace to the moulds.

The charge should not be poured through the furnace door, if this door has to be opened during pouring. It is much more convenient to pour the silver through a separate taphole, which can be lined and kept closed by a plug made from an electrode stump.

The travel of the metal from spout to mould should be as short as possible and all chilling should be prevented. With proper arrangements I have experienced no trouble due to chilling and skin forming during pouring and casting.

If an intermediate receptacle is used between spout and mould, same should have a cover and should be thoroughly preheated. Any metal left in this vessel should be poured out before taking the next charge from the furnace. All moulds should be smoked and warmed up to about 204° C. (400° F.).

A complete and efficient silver melting equipment is illustrated in Fig. 1 and its mode of operation is as follows:

"A" is a lip-tilting electric furnace, which is charged through furnace door "B." Before charging the furnace it should be preheated to about 1093° C. (2000° F.).

If necessary, enough powdered charcoal is added to give the right atmosphere. As soon as the silver begins to melt, the iron block is put in the bath and the metal is heated up to about 1314° C. (2400° F.), but not higher. If no pyrometer is available, tests are taken. These consist in pouring a spoonful of metal into water. The right temperature is indicated when the granules thus produced are round and do not hang together. If flat pieces appear the metal is too cold.

For sterling silver, the water is then poured off the test and the gobules are annealed over the furnace door. If they show a bronze tarnish, the metal is right for pouring.

The furnace is then tilted and the metal discharged through the specially lined taphole and spout placed directly beneath the door.

The charging door remains closed and as the taphole is of small diameter, it is covered by metal during the pour and no air, therefore, gets into the furnace.

The metal flows from the spout into a lined pot or crucible hung in front of the furnace. It is provided with a cover and sets into a ring so that the entire pot is removable. Before using,

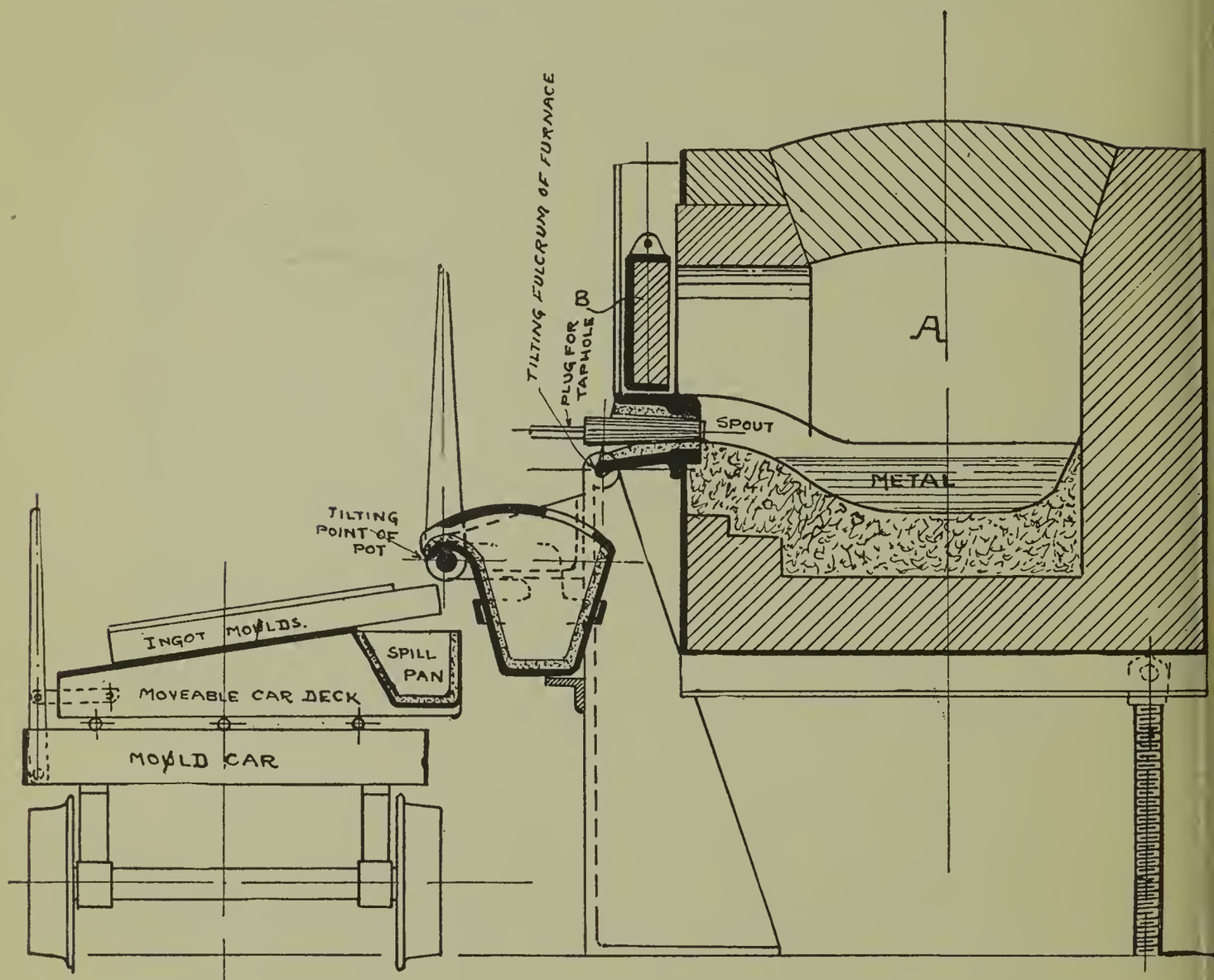


FIG. 1

it should be thoroughly preheated and it should be of sufficient capacity to hold enough metal to fill one or more moulds. The pot is also lip-tilting and is worked by a lever. In front of this pot runs a mould car provided with a deck, which can be moved back and forth. Under the pouring tops of the moulds is provided a spillpan, to collect all spillings and into same is also poured all surplus metal from the pot.

The operation of this device is very simple and no charcoal will be needed outside of the furnace.

The furnace lining can be either of silica brick or firebrick, with a hearth of gannister or carborundum. The hearth material should be wetted down with silicate of soda, tightly rammed in and thoroughly sintered. The life of such a lining will be almost indefinite.

As already stated, the furnace used by the writer was a modified 100 KVA Rennerfelt of 10,000 oz. capacity, with a total production of 60,000 oz. of silver per 8 hours.

The metal losses on the runs made were not quite conclusive, but averaged about 1 oz. per 1000 oz. melted.

The furnace was newly lined and most of the losses must be attributed, therefore, to absorption. I am fully convinced that these losses will be cut in half and even down to one quarter after the furnace has been in use a little longer. The power consumption per ton of silver averaged 330 KWH with preheating and 260 KWH without preheating. The average consumption per 1000 oz., therefore, is about 12 KWH.

The cost of melting and casting 1000 oz. of rolling mill silver were as follows:

| | |
|---|---|
| Loss ½ oz. per 1000 | $0.25 |
| Power 12 KWH at 2 cents | 0.24 |
| Labor, melting and pouring | 0.20 |
| Charcoal at 2 cents per lb | 0.0025 |
| Electrodes | 0.05 |
| Refractories | 0.02 |
| Heating ladles and moulds | 0.02 |
| Total | $0.7725 |

If silver losses are reduced to 1/4 oz., the total cost then would be 65 cents.

The silver produced by these methods was thoroughly tested and compared with standard grade crucible silver and the results are given in a letter from the Gorham Company.

"June 21, 1921.

Mr. H. A. DeFries,
Consulting Engineer,
15 Park Row, New York City.

Dear Sir: Answering your letter of June 12th, in which you ask us for information concerning the results which we obtained from tests of silver made in the Rennerfelt electric furnace.

Will advise that in the drawing operations, which furnished a very severe test for the silver, it proved much more satisfactory than the silver produced by the crucible method of melting.

The spinning, stamping and hammering tests also showed it to be more ductile and more easily handled than our regular stock, as it seemed to have a much finer grain and would stand more punishment than the silver melted in the crucible furnaces.

As to the tensile strength, would say that while it showed favorably, it was not a test that we would care to say much about, as the test was made under very unfavorable conditions from a drawn part which had been cut crosswise of the grain of the stock from which the specimen was drawn, and I don't think this test would be fair in either case.

Yours very truly,

(Signed) G. H. NORTH,
Superintendent."

An extreme test for deep stamping and forging was made at the same time on seven sheets of crucible silver and seven sheets of electric silver, with the result that six sheets of the crucible silver were destroyed, whereas the electric silver came out 100 percent perfect. A spinning test on the same number of sheets showed that all crucible silver failed, before any splitting or warping of the electric silver took place.

The last question to be considered is the elimination of impurities which may get into the silver, especially if old metal and scrap are remelted. These impurities consist mainly of small particles of German silver, but seldom more than a fraction of one percent. The zinc from these impurities can be eliminated by distillation. The surplus of copper can be compensated by adding sufficient fine silver to get the right assay standard. Nickel, however, cannot be removed, but will be present in such minute quantities that it will not affect the standard in a detrimental way.

Most silver melting plants possess a complete refining equipment and generally the melting furnace is not called upon to do much of this work.

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## DISCUSSION.

C. S. WITHERELL[1]: May I ask what kind of iron the author uses?

[1] Metallurgical Engineer, New York City.

E. F. NORTHRUP[2]: I happen to have been the witness of the melting of over a million ounces of silver in the electric furnace. The melting was carried on under the most varied conditions, to determine the best procedure for getting rid of the small gas blow holes which are prone to show in the silver when this is rolled down into a thin sheet. The melting was carried on in an Acheson graphite crucible, without any lining on the inside. It was brought to a high superheat (1205° C.), and on other occasions to a temperature at which it would just pour. Different charges were covered with different materials as bone, and salt, and charcoal, but blow holes nearly always appeared. It was found, however, that when some of the silver was poured into a crucible and this filled crucible was put into an oil-fired furnace and held there for awhile, the pour made directly from this crucible generally yielded good silver. Experiments were varied in many ways, using lined and unlined graphite crucibles, and the manner of pouring was varied in many ways.

The best opinion resulting from this experimentation was that the injury to the silver occurred during the time that it was passing from the crucible of the electric furnace into the mold. Changes were made so that the silver ran over an extremely short spout instead of a rather long one as before. It was then found that whether the pouring temperature was very high or just a little above the melting temperature, silver which was fairly satisfactory was obtained.

Much could be said on this subject, and I am not offering any solution of the problem of how to pour uniformly good silver. I do wish to say, however, that people who have had vast experience and who have been in the silver business for years and know what they are talking about, find the problem of pouring good silver still puzzling, and that it is almost beyond their ability to say just what are the causes of good and bad silver. It is, however, proved beyond a doubt that the pour must be made over a short spout, and that the manner in which the pour is made has the greatest bearing on success in getting good silver.

COLIN G. FINK[3]: I might add that after using this block of iron for a number of times and taking it out and examining it,

[2] Vice-Pres. and Technical Adviser, Ajax Electrothermic Corp., Trenton, N. J.
[3] Consulting Electrometallurgist, New York City.

it presented a very black surface, and looked as though it had been weather-worn or been exposed to the action of water in a brook for many years, this peculiar erosion showing that besides controlling temperature there is an actual control of the oxygen content in the silver.

J. W. RICHARDS[4]: I can make a general remark about the casting of metals, which applies to silver as well as to steel and others. When you cast a liquid metal from a ladle, the falling stream of metal acts by suction to draw air in with it. The amount of oxidation under those conditions may be very large in a small distance of fall, and the air is carried down into the liquid metal and churned into it, as if you were to pour the water out of this pitcher into a glass you could see the globules of air carried down.

If you consider dropping, as is sometimes done, a stream of metal five and six feet into an ingot mould, you can see the extreme conditions for oxidation of the metal in the act of pouring. I think that emphasizes the point Dr. Northrup brought out, that there is little use of taking care of the metal before you pour it, if you are going to pour it loosely under conditions where it can oxidize rapidly.

[4] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# THE ELECTRIC FURNACE MELTING OF NICKEL SILVER.[1]

By F. C. Thompson, D.Met., B.Sc.[2]

Abstract.

The author presents advantages of the externally heated electric furnace for nickel-silver melting, insofar as (a) loss of zinc is reduced to less than 1 percent, (b) occlusion of gases is minimized, and (c) a tougher alloy results owing to less carburization. [A. D. S.]

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Of all types of electric furnace for the melting of steel, the arc is the one which has attained most success. In the melting of such alloys as cupro-nickel this success has also been attained within the realm of non-ferrous metallurgy. Such a furnace as the Héroult is eminently suited for this alloy, and purification and in particular decarbonization is an accomplished fact. Very large admixtures of scrap can be made to the charge and by an initial oxidizing stage under a slag consisting largely of oxides of nickel and copper, followed by a final deoxidizing one in which the first slag has been removed and for it one consisting of a little anthracite, limestone chippings and fluor spar substituted, exceedingly good material is produced.

When dealing with nickel-silver, however, this type of furnace ceases to be very useful as a result of the large volatilization of zinc around the electrodes. This results in high melting losses, a tendency, unless the chemical control is accurate, to irregularity of composition and an atmosphere in the melting shop which is far from satisfactory, although with an absolutely adequate system of ventilation this latter objection might be more or less overcome. The author's experience, which, however, has been

[1] Manuscript received August 23, 1921.

[2] Professor at Manchester University, England.

somewhat limited on these lines, has not been satisfactory, but only where all the constituents of the melt are essentially non-volatile is the arc furnace, in his opinion, satisfactory. Certainly, however, where this condition is satisfied, this type of furnace is capable of yielding very promising results.

These facts lead to the conclusion that only electric furnaces of the induction type, or those in which the heating is by resistance in or around the walls, are of real utility. Experiments carried out in a small Kjellin induction furnace have not yielded results which possess much promise, so that resistance furnaces alone would appear to be satisfactory. These have already proved themselves efficient with melting of brass, and though the higher melting point of nickel-silver introduces a further difficulty there is, so far as the author knows, no inherent reason to doubt that nickel-silver can be satisfactorily melted in this type of furnace.

One may, therefore, conclude with a fair degree of certainty that the electric furnace melting of nickel-silver in a pure resistance furnace is a possibility. How far it may be commercially advisable to use this method is one of a purely economic character which will quite obviously depend on local conditions and no dogmatic opinion can be given.

We may now proceed to the discussion of the advantages, if any, from the purely technical point of view, possessed by electric furnaces for this purpose.

### (a) *Loss of Zinc.*

The loss of zinc in crucible melting should not exceed somewhere about 1 percent. In a closed electric furnace of the resistance type this figure should not be exceeded and may be substantially reduced.

### (b) *Occlusion of Gases.*

How far gases, other than those which may introduce sulphur or oxygen into the melts, exert a harmful influence on nickel-silver is not known with any certainty, but to the author no such influence is known. One would be inclined, however, to expect that the lower the volume of occluded hydrogen, nitrogen, etc., the better. Where sulphurous gases are concerned it is emphatically the case that their influence in the metal is bad. All crucibles

are permeable to gases in the melting holes and sulphur from the coke, etc., can be, and actually is, transmitted through the walls of the crucibles and absorbed by the metal. The electric furnace possesses here one of its greatest advantages since much of the deterioration of the metal even after repeated remeltings as scrap is reduced to a minimum.

Oxidation also certainly occurs in crucible melting even under the best conditions, although by suitable furnace regulation it may be minimized. The author has shown[3] that oxygen in nickel-silver occurs as minute globules of zinc oxide which probably increase the tendency for the metal to crack during annealing or stamping. Electric furnace melting should certainly lead to no great degree of oxidation, while under good conditions this may perhaps be reduced and with a suitable covering of an inactive slag the almost inevitable access of oxygen through charging doors, etc., should be prevented from entering the melt. The burning of a reducing gas in the furnace will also minimize this effect.

### (c) *Carburization.*

Nickel and the nickel alloys show a tendency to absorb carbon, in particular when molten, which is parallel to the tendency possessed by iron. The carbon, which normally occurs as $Ni_3C$ exerts in that form very little, if any, harmful influence on the mechanical properties, and may even enhance these, yielding a metal which is both stronger and tougher. The conditions are, however, very different if the nickel carbide has decomposed with the precipitation of graphite, a tendency to which it is specially prone when annealed after cold work. This tendency is due to the exothermic nature of the decomposition of the carbide.

The author, in conjunction with Mr. W. R. Barclay[4] investigated this matter in the allied alloy cupro-nickel, and found that above about 700°C. graphitization occurs in highly carburized materials resulting in intense intercrystalline brittleness. In nickel-silver itself the author has shown that graphitization occurs preferentially at the surface of the specimen where the

[3] Trans. Chem. Soc., 1914, **105**, 2342.
[4] Soc. Chem. Ind., 1919, XXXVIII, p. 130-T.

increase of volume associated with the change can be most readily accommodated.

Graphitization is a very real source of trouble in nickel-silver for cutlery, etc., since under ordinary conditions a considerable amount of scrap has to be remelted and where this is done in the crucible a gradual accumulation of carbon occurs, which will in time lead to the trouble under discussion. To prevent this it is necessary to add to each melt an appreciable quantity of the more expensive virgin metal to dilute the carbon and thus maintain it within safe limits. Melted in an electric furnace with a non-carbonaceous slag this carbon increase, inevitable in the case of crucible melting, should be capable of considerable reduction. In such cases the amount of scrap which can be dealt with will be much larger and metal which is not liable to brittleness due to the precipitation of graphite on annealing produced.

The following figures taken from a paper by the author illustrate well the avidity with which the molten alloy will absorb carbon from the crucible and the deleterious effect of such absorption on the annealed material.

| Crucible | Arnold Alternating Stress No. |
|---|---|
| "Black Lead" | 842 |
| Clay | 904 |

The increased "toughness" of the alloy (10 percent nickel) melted under the less carbonizing conditions of the clay crucible will be evident. The latter conditions will correspond the more nearly to those in electric furnace melting.

In the author's opinion, therefore, where local conditions render it economically advisable the electric furnace of the external heating type possesses technical advantages especially where large quantities of scrap require to be remelted in (1) minimizing the accumulation of sulphur and carbon and thus (2) in reducing the amount of virgin metal required for the charge.

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## DISCUSSION.

H. M. St. John[1]: In discussing the arc furnace, the author says "these facts lead to the conclusion that only electric fur-

[1] Vice-Pres. and Service Mgr., Detroit Electric Furnace Co., Detroit, Mich.

naces of the induction type, or those in which the heating is by resistance in or around the walls, are of real utility." That may be true, so far as any stationary type of arc furnace is concerned. It seems to me, however, that the type of arc furnace which is suitable for melting brass, containing as much as 30 or 40 percent zinc, is equally suitable for melting nickel silver. The rocking, or oscillating, arc furnace, which constantly stirs its charge, and continually presents a new surface of metal to the arc radiation, should receive consideration for this work.

H. W. GILLETT[2]: I have made experimental heats of "nickel silver" in a laboratory rocking arc furnace. From examination of the ingots produced the results appeared satisfactory.

While the results given on the Arnold alternating stress tests cited in the paper may, and probably do, lead to a correct conclusion, it is unsafe to depend on tests made as the Arnold test is, at a stress that produces permanent set in the test piece, as a criterion of endurance at working stresses. Tests made over a wide range of stresses, and within the elastic limit, are necessary before any certain conclusions can be drawn.

F. C. THOMPSON (*Communicated*): The questions of the satisfactory melting of brass and of nickel-silver are not quite identical. The latter alloy is often called on to stand much severer stresses during manufacture and use, and since it has less ductility the effects of bad melting are the more serious. There is, however, a good deal to be said for the type of furnace in which the arc is in movement, and I am glad the writers have drawn attention to it.

I can not agree that the Arnold test is unsafe in the investigation of the nickel-silvers. The very fact that Mr. Gillett has mentioned that the stresses are above the elastic limit, is more a point in its favor than against it. During stamping, spinning, etc., a great deal of plastic work is done on the metal, and a test which will give an idea of the resistance of the alloy to such work is from the manufacturer's point of view of the greatest use.

[2] U. S. Bureau of Mines, Morse Hall, Ithaca, N. Y.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# ALUMINUM-COPPER ALLOYS.[1]

By Robert J. Anderson.[2]

## Abstract.

A brief discussion of the manufacture, properties and uses of the commercial aluminum-copper alloys employed in the United States. The light alloys, intermediate alloys, and heavy alloys are treated, the constitution of the aluminum-copper system is touched upon, and the metallography and heat treatment of the alloys are briefly touched upon. Casting, forging and rolling alloys are considered in detail. The general properties of the alloys, including specific gravity, tensile properties and the effect of pouring temperatures thereon, and corrosion are taken up, while the mode of manufacture is discussed briefly. The various uses of the alloys in commercial work are indicated, and a selected bibliography to the literature is appended.

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## INTRODUCTION.

The object of the present paper is to give briefly and in a broad way certain general information with regard to the manufacture, properties, and uses of the commercial aluminum-copper alloys employed in the United States. A secondary object of the paper is to indicate some of the scientific problems to be solved in the engineering utilization of the alloys as well as to point out some directions for future development work. The aluminum-copper alloys have been chosen for discussion here because they are the most important commercially from the viewpoint of amount consumed among the various commercial light aluminum alloys. To the United States, the importance of the aluminum-zinc alloys is

[1] Published by permission of the Director, U. S. Bureau of Mines. Manuscript received August 5, 1921.

[2] Metallurgist, U. S. Bureau of Mines, Experiment Sta., Pittsburgh, Pa.

quite small, since the uses of these alloys are small. Aluminum-manganese, aluminum-magnesium, aluminum-copper-manganese, aluminum-copper-tin, and aluminum-copper-zinc alloys are used only to a subordinate extent in this country. There are several good reasons for the industrial preference of light aluminum-copper alloys over other light aluminum alloys, as will be pointed out later, but for the moment it is sufficient to know that about 98 per cent of the total output of aluminum-alloy sand castings is made in the alloy containing about 92 percent aluminum and 8 percent copper (known in trade parlance as No. 12 alloy), and in related aluminum-copper alloys containing from 4 to 14 percent copper and remainder aluminum.

The aluminum-copper alloys have been investigated more fully in their scientific, metallurgical, and practical aspects than have other light aluminum alloys, and a large mass of literature has now accumulated dealing with the constitution of the aluminum-copper system, the metallography of the alloys, methods for preparation, properties, uses, and applications. Much investigative work remains to be done, however, before the metallurgy of the alloys is placed upon the same basis, as to knowledge, as the metallurgy of steel. In view of the great importance of the light aluminum alloys, both aluminum-copper alloys and other aluminum alloys, as engineering materials of construction, it cannot be emphasized too strongly that a broad research program is urgently needed in this field. The Bureau of Mines, in its investigative work in the metallurgy of aluminum, has made a number of investigations dealing with the manufacture and utilization of the light aluminum-copper alloys to which reference is made in later paragraphs. This paper is issued as a contribution to the literature of the metallurgy of the light aluminum alloys, and it is hoped that the information given will be found of interest and value to the nonferrous alloy industry. While it will not be possible to cover the ground in a detailed way in a short paper like this one, still the more important features of the commercial production and utilization of the alloys may be dealt with. The present paper is devoted principally to a discussion of the light alloys, and the intermediate alloys and the aluminum bronzes are dealt with only in a perfunctory way.

## ALUMINUM-COPPER ALLOYS IN GENERAL.

Binary alloys of aluminum and copper are among the oldest aluminum alloys known from the standpoint of experimentation, and aluminum bronze was one of the first aluminum-containing alloys produced for commercial use. The introduction of light aluminum-copper alloys, as they are known today, for casting purposes, is, however, relatively recent in point of time. In the United States, the employment of these alloys in foundry work has been growing steadily in contradistinction to the aluminum-zinc alloys whose popularity has waned. The vicissitudes experienced by the aluminum-zinc alloys have been somewhat peculiar, but the merest mention of this matter must suffice here. From the viewpoint of the foundrymen, the aluminum-copper system is of special interest since it embraces light casting alloys, intermediate alloys (the so-called hardeners or rich alloys of foundry practice), and aluminum bronze.

The commercially useful aluminum-copper alloys include certain ones at either end of the series, as well as some intermediate alloys and aluminum bronze. At the aluminum end of the system, alloys containing up to about 14 percent copper and remainder aluminum are employed for various purposes, and these fall in the class of light casting alloys. Two intermediate alloys find commercial use: viz., an alloy containing about 33 percent copper and 67 percent aluminum, and an alloy containing about 50 percent copper and 50 percent aluminum, known as 33:67 and 50:50 alloy, respectively. These intermediate alloys are employed solely for making fixed additions of copper to aluminum as in the preparation of the 92:8 Al-Cu alloy, or of aluminum to copper as in the preparation of aluminum bronze. The alloys at the copper end of the series fall in the class of heavy aluminum alloys, and they are known generally as aluminum bronzes. In reality, however, commercial aluminum bronzes are now generally ternary copper-aluminum-iron alloys.

It has been indicated above that the light aluminum-copper alloys are used very largely for the production of sand castings in the United States. In England, on the other hand, certain aluminum-zinc and aluminum-copper-zinc alloys are favored, and England has been foremost also in the development of these and

other aluminum alloys. In the United States, when so-called "aluminum castings" are mentioned[3], the 92:8 Al-Cu alloy is generally understood to be used. The actual limits of composition for this alloy are relatively close, usually from 7 to 8.5 percent copper and remainder aluminum, although in foundry work the total impurities, particularly iron, may be, and are, quite appreciable at times. When any particular departure is made from these limits, such as would obtain with a 4 or a 12 percent copper-aluminum alloy, it means simply that the 92:8 Al-Cu alloy is not suited for the purpose. The greater part of the light aluminum-copper alloys made today is put into sand castings, but an increasing amount is going into die castings and into permanent-mold castings. A subordinate amount is rolled and forged.

The aluminum-alloy casting industry has grown to large proportions in the past ten years, and there are now over 2,000 foundries in the United States in which aluminum-alloy castings are produced. According to the latest data gathered by The Foundry, there are 2,169 foundries[4] in the United States in which light aluminum-alloy sand castings are made. As has been indicated No. 12 alloy is employed principally, and the use of special alloys is confined in general to the large shops. Certain aluminum-zinc and aluminum -copper-zinc alloys are cast, however, by some small foundries.

## CONSTITUTION OF THE ALUMINUM-COPPER SYSTEM.

The aluminum-copper system has been studied at considerable length, notably by Guillet[5], by Curry[6], by Carpenter and Edwards[7], and by others. Especial details of the constitution of the aluminum bronzes (alloys at the copper end of the system) have received attention at the hands of a number of investigators, particularly

[3] Practically no castings in substantially pure aluminum are made, and the term "aluminum castings" is a misnomer which causes much confusion.

[4] Anon., Growth marks reconstruction era, The Foundry, 1920, 48, 853-858.

[5] Guillet, L., Étude théorique et industrielle des alliages de cuivre et d'aluminium, Rev. de Mét., 1905, 2, 567-588.

[6] Curry, B. E., The constitution of the aluminum bronzes, Jour. Phys. Chem., 1907, 11, 425-436.

[7] Carpenter, H. C. H., and Edwards, C. A., On the properties of the alloys of aluminum and copper; eighth report to the alloys research committee, Proc., Inst. of Mech. Engrs., 1907, 72, 57-269.

by Brueil[8], by Barrée[9], by Robin[10], by Hanemann and Merica[11], by Portevin[12], by Andrew[13], and most recently an extensive investigation of the subject has been undertaken by Greenwood[14]. The metallography of the alloys has been worked out in considerable detail, particularly at the copper end of the series. The equilibrium diagram published by Carpenter and Edwards agrees well with that shown by Guillet, but recent studies by Mercia[15] and his collaborators indicate that the solubility of $CuAl_2$ in aluminum is different than that given in the earlier investigations.

Considerable similarity exists in the aluminum-copper and in the copper-tin systems, particularly as regards intermediate compounds and metallographic constituents. Three compounds exist in the aluminum-copper series corresponding to the formulae $Cu_4Al$, $Cu_3Al$, and $CuAl_2$. $Cu_4Al$ does not crystallize from the liquid but appears as a recrystallization out of a homogeneous solid. Excluding constituents that may be obtained by quenching or chilling, Carpenter and Edwards have found six different ones, *viz., alpha, alpha', beta, gamma, delta,* and *eta* (Fig. 1). While it is not necessary to discuss the equilibrium diagram of the aluminum-copper system here, the curve shown in Fig. 1 may be included for reference. Details may be had by consulting the works cited.

### *Metallography of the Aluminum-Copper Alloys.*

Microscopic studies have been made of the alloys in the aluminum-copper system in connection with investigations of the equilibrium diagram, and especial study has been given to the structural changes arising on heat treatment in the case of the aluminum

[8] Brueil, P., Constituant spécial obtenu dans la trempe d'un bronze d'aluminium, *Compt. Rend.,* 1905, **140**, 587-590.

[9] Barrée, M., Sur les points de transformation des alliages cuivre-aluminum (étude de la variation de la résistance électrique avec la temperature), *Compt. Rend.,* 1909, **149**, 678-681.

[10] Robin, F., Sur les constituants en aiguilles des alliages. Bronzes d'aluminum et étain spéciaux, Bull. de la Soc. d'Encourag. par l'Industrie Nat., 1913, **119**, 12-41.

[11] Hanemann, H., and Merica, P., Über Kupfer-Aluminium-Legierungen mit 84 bis 90 percent Kupfer, Intern. Zeit. für Metallog., 1913, **4**, 209-227.

[12] Portevin, A., Sur le constituant beta des bronzes d'aluminium, Intern. Zeit. für Metallog., 1913, **4**, 257-260.

[13] Andrew, J. H., Some experiments upon copper-aluminum, Jour. Inst. of Metals, 1916, **13**, 249-260.

[14] Greenwood, J. N., The constitution of the copper-rich aluminum-copper alloys, Jour. Inst. of Metals, 1918, **19**, 55-100.

[15] Merica, P. D., Waltenberg, R. G., and Freeman, Jr., J. R., Constitution and metallography of aluminum and its light alloys with copper and with magnesium, Bureau of Standards Sci. paper No. 337, August 16, 1919; and Bull. Am. Inst. of Min. and Met. Engrs., No. 151, July, 1919, pp. 1051-1062.

bronzes. At the aluminum end of the series, considerable microscopic work on the light aluminum-copper alloys has been done by Hanson and Archbutt[16] at the National Physical Laboratory, by Merica[17] and his collaborators, by Wills[18], and by the writer[19, 20, 21]. The commercial application of metallography to aluminum-alloy manufactures as a method of test and control of quality has not yet been widely employed in practice, and in reality a working metallography for the aluminum alloys is still to be evolved.

While the heat treatment of light aluminum-copper alloy castings is just now being developed, this can be controlled only by metallographic methods, and this development seems to be of much promise. The effects of annealing and quenching (heat treatment) upon the properties of aluminum-copper-alloy sand castings have been examined in a preliminary way[22, 23].

Referring now briefly to the microscopic constituents found in commercial light aluminum-copper alloys, there may be considered ordinary No. 12 alloy. When copper is added to aluminum, the intermetallic compound $CuAl_2$ is formed; this compound is soluble in the solid state in aluminum up to about 4 percent at 500° C., but the solubility varies considerably with the temperature, being apparently only about 1 percent at the ordinary temperature. With increasing copper, over 4 percent, an eutectic is formed between $CuAl_2$ and the aluminum-$CuAl_2$ solid solution. $CuAl_2$ is white and bright in unetched microsections, but it may be colored by suitable etching reagents. Iron when present in aluminum-

[16] Hanson, D. and Archbutt, S. L., The micrography of aluminum and its alloys, Jour. Inst. of Metals, 1919, **21**, 291-304.

[17] Merica, P. D., Waltenberg, R. G., and Freeman, Jr., J. R., Constitution and metallography of aluminum and its light alloys with copper and with magnesium, Bureau of Standards Sci. paper No. 337, August 16, 1919; and Bull. Am. Inst. of Min. and Met. Engrs., No. 151, July, 1919, pp. 1051-1062.

[18] Wills, L. J., The micrography of aluminum and of some aluminum alloys, with special reference to the effect of iron and silicon, Jour. Birmingham Met. Soc., 1919, **7**, 475-499.

[19] Anderson, R. J., Metallography of aluminum; preparation and etching of microsections, Met. and Chem. Eng., 1918, **18**, 172-178.

[20] Anderson, R. J., Castings of light aluminum alloys, The Iron Age, 1921, **107**, 433-436.

[21] Anderson, R. J., Ferric sulphate as a new etching reagent in the metallography of aluminum, The Metal Ind., 1921, **19**, 69-70.

[22] Merica, P. D. and Karr, C. P., Some tests of light aluminum casting alloys—the effect of heat treatment, Bureau of Standards, Tech. paper No. 139, October 24, 1919.

[23] Jeffries, Z., and Gibson, W. A., Heat treatment of aluminum-alloy castings, Bull. Am. Inst. of Min. and Met. Engrs., No. 153, September, 1919, pp. 2493-2512.

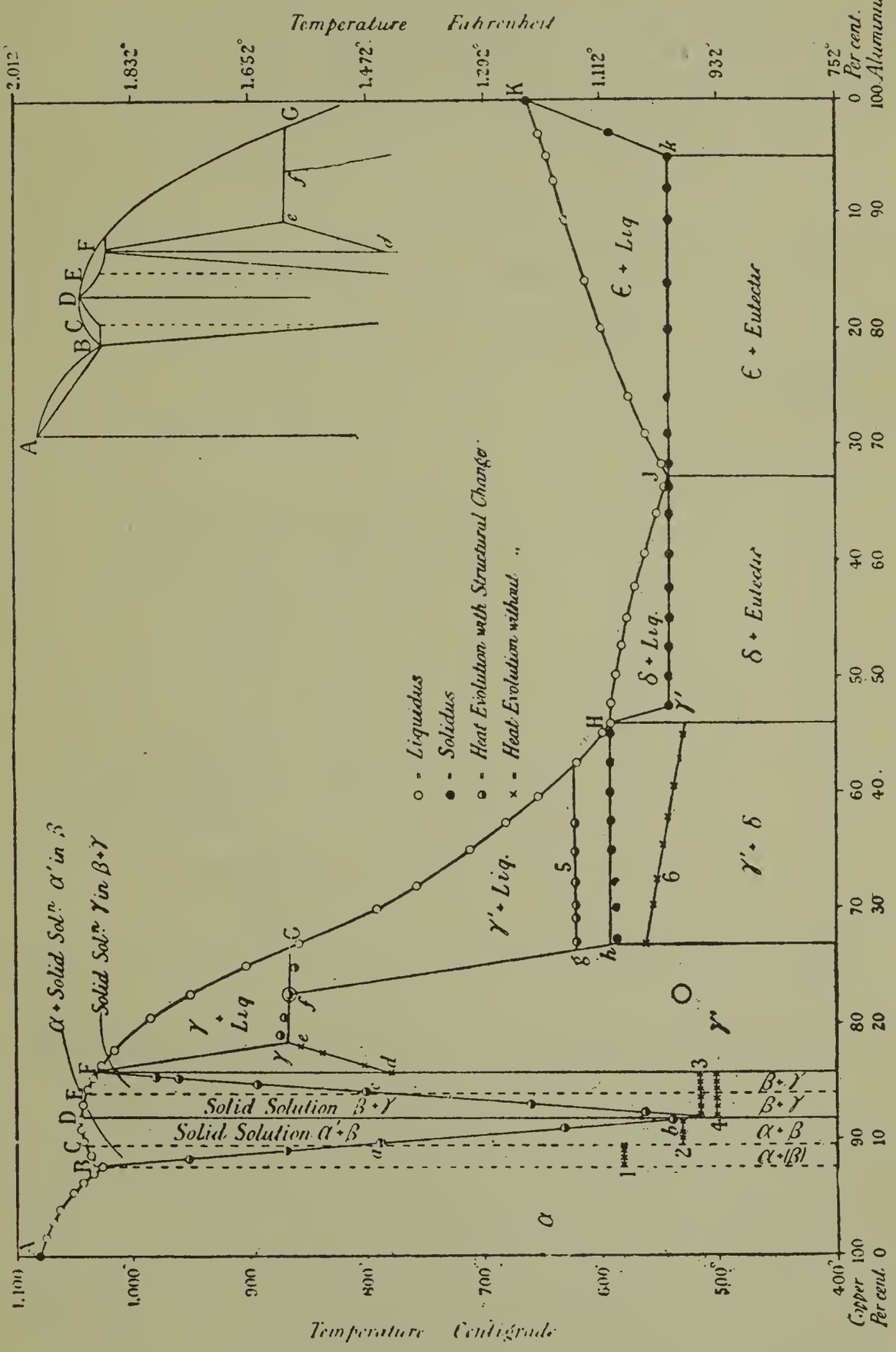


FIG. 1. Equilibrium diagram of the aluminum-copper system (Carpenter and Edwards.)

copper alloys, as it normally is, forms the compound $FeAl_3$, which is practically insoluble in the solid state. With 0.50 percent iron present, the $FeAl_3$ separates out in the form of white needles. The photomicrographic aspects of the various light aluminum-copper alloys have been shown in the papers cited, and they need not be reproduced here.

TABLE I.

*Composition of Industrial Light Aluminum-Copper Alloys.*

| Approximate Composition Elements Percent | | Used for |
|---|---|---|
| Al* | Cu | |
| 98 | 2 | Rolling, forging and sand casting |
| 97 | 3 | Rolling, forging and sand casting |
| 96 | 4 | Sand casting |
| 95 | 5 | Sand casting |
| 94 | 6 | Sand casting |
| 93 | 7 | Sand casting |
| 92 | 8 | Sand casting, die casting and permanent mold casting |
| 90 | 10 | Sand casting, die casting and permanent mold casting |
| 88 | 12 | Sand casting, die casting and permanent mold casting |
| 86 | 14 | Sand casting |

* This refers to commercial aluminum containing the usual impurities in subordinate amounts.

COMPOSITION OF COMMERCIAL LIGHT ALUMINUM-COPPER ALLOYS.

In actual foundry practice, and elsewhere, the chemical composition of light aluminum-copper alloys employed for particular purposes is very variable indeed. In fact, alloys containing from 2 to 14 percent copper and remainder aluminum are used for sand castings. A number of fairly definite compositions are in use, and definite alloys have been developed for particular purposes. Thus, the alloys given in Table I are employed commercially.

From the commercial standpoint, copper is a fairly cheap metal to be used for alloying with aluminum, and while not so cheap as zinc, it has the advantage that less needs to be employed to furnish fairly desirable physical properties in the resultant alloy. However, the specific gravity of the light aluminum-copper alloys is less than that of the light aluminum-zinc alloys, on the comparative basis of two alloys of each class both having good physical properties. It is largely for these reasons, and also because the aluminum-zinc alloys have a rather poor reputation among engineers, that the light aluminum-copper alloys are favored in the United States.

To be precise in statement, it is necessary to point out that actual binary aluminum-copper alloys do not exist in commercial practice, and industrial alloys always contain at least the usual impurities in the aluminum used, *i. e.*, iron and silicon, in small amount. Other impurities often found in commercial aluminum-copper alloys include magnesium, manganese, tin, and zinc. Ordinarily, high-grade electrolytic copper is used for the preparation of aluminum-copper alloys, and impurities arising from the copper are practically *nil.* The effects of impurities, either alone or together, upon the properties of various aluminum-copper alloys is a question of much interest, and while some attention has been paid to this, the subject is open to thorough investigation.

### *Aluminum-Copper Casting Alloys.*

The alloy containing 7-8.5 percent copper and remainder aluminum has been used for many years for general automotive and other castings. Practically any of the alloys within the limits 2 to 14 percent copper can be sand-cast as a foundry proposition, but shrinkage difficulties are always troublesome in the alloys lean in copper. Probably, the best all-around mechanical properties are provided by the 92:8 Al-Cu alloy, among the light aluminum-copper alloys, but this alloy is too brittle for some purposes, and the alloy containing 94-95 percent aluminum and 6-5 percent copper may be used instead. In connection with automotive work, alloys containing 9-10.5 percent copper and 11-13.5 percent copper (remainder aluminum) have been developed for special purposes, the former being used for pistons and the latter for manifolds.

The alloy containing 96 percent aluminum and 4 percent copper is employed to some extent in the United States and in Europe for castings where more ductility is required than the 92:8 Al-Cu alloy provides; the former alloy is used in the United States in the manufacture of cast cooking utensils and cast parts for utensils. The 92:8 alloy is a good alloy from the foundry point of view; the casting plants have had long experience with it; and it is the best known and most widely used. Probably, the first aluminum-rich alloy employed in foundry work was one containing about 6-8 percent nickel and remainder aluminum[24]; this was known as No. 12 alloy. When the nickel was replaced by copper, the aluminum-copper alloy resulting was then called No. 112, and also No. 12, and it is now not unusual in commercial work for small amounts of magnesium, manganese, or nickel to be added to the 92:8 Al-Cu alloy.

### *92:8 Al-Cu Alloy.*

The alloy containing about 92 percent aluminum and 8 percent copper can be depended upon to have an ultimate strength of 18,000 pounds per square inch and an elongation of 1-1.5 percent in a two-inch length. These figures refer to sand-cast bars, cast coupon or separately. It is evident from these figures that the alloy is neither remarkably strong nor ductile. Strictly speaking, the commercial No. 12 alloy is not a simple binary alloy in most foundries because of the presence of appreciable amounts of impurities. When the iron content is high, and iron is present frequently in amount up to 1.75 percent in actual castings, the alloy should be regarded properly as a ternary aluminum-copper-iron alloy. This distinction is regarded often as academic from the foundry viewpoint, but it really is not because increasing amounts of iron markedly affect the properties of the alloy. As a matter of fact, in sand castings made in this alloy, particularly when iron-pot melting practice[25] is used, the iron content will be 1 percent or more. In the case of die castings, the iron content may be as high as 3 percent. The fact that the iron percentage is high may be attributed to the use of high iron scrap in the melting

[24] Anderson, R. J., Special and commercial light aluminum alloys, Bureau of Mines, War Minerals Investigations Series No. 14, April, 1919, p. 13.

[25] Anderson, R. J., Iron-pot melting practice for aluminum alloys, The Metal Ind., 1921, 19, 189-190; 246-247; and others to appear (serial).

charge, or to iron-pot melting practice, or to both. Secondary No. 12-alloy pig, as marketed by smelters, may contain considerable iron, and unless melting materials are purchased on chemical analysis, excluding all stock high in iron, the alloy cannot be expected to approach 92:8 Al-Cu in composition. In order to indicate the actual composition of No. 12-alloy castings, a few chemical analyses of control samples taken in the production of crankcases for the 12-cylinder Liberty aviation engine as cast under

TABLE II.

*Control Analyses of Liberty Motor Crankcases.**

| Sample Number | Elements, percent | | | |
|---|---|---|---|---|
| | Al† | Cu | Fe | Si |
| 1 | 90.52 | 8.16 | 1.04 | 0.28 |
| 2 | 90.50 | 8.21 | 0.99 | 0.30 |
| 3 | 90.44 | 8.20 | 0.96 | 0.40 |
| 4 | 90.66 | 8.06 | 0.92 | 0.36 |
| 5 | 90.69 | 8.07 | 0.94 | 0.30 |
| 6 | 90.88 | 7.87 | 0.93 | 0.32 |
| 7 | 90.47 | 7.96 | 1.15 | 0.42 |
| 8 | 90.61 | 8.06 | 0.98 | 0.35 |
| 9 | 90.24 | 8.24 | 1.14 | 0.38 |
| 10 | 90.32 | 8.24 | 1.12 | 0.32 |
| 11 | 90.16 | 8.19 | 1.29 | 0.36 |
| 12 | 90.30 | 8.11 | 1.21 | 0.38 |
| 13 | 90.80 | 8.21 | 0.72 | 0.27 |
| 14 | 90.83 | 8.00 | 0.91 | 0.26 |

* Analyses by Bureau of Aircraft Production.
† Aluminum, by difference.

the specifications of the Bureau of Aircraft Production, may be considered. The analyses shown in Table II represent results on samples selected at various intervals during about three-months' production.

In addition to iron as an impurity, magnesium may be present in No. 12 alloy, since this metal is added occasionally to heats in foundry practice. So-called No. 12 alloy pig (secondary) may be very variable as to composition when run down from miscellaneous scrap, and, in addition to copper, iron, and silicon, it often contains considerable amounts of zinc and manganese, as well as

magnesium in subordinate amounts. Tin and lead may be present also in small percentages. So-called "casting aluminum" made by melting miscellaneous scrap may masquerade at times in the trade as No. 12 alloy. In this material, zinc may be present in amount up to 5 percent or more, and it may contain up to 0.75-1 percent manganese.

### *Aluminum-Copper Forging Alloys*

Not an important amount of any light aluminum-copper alloys is forged as a commercial proposition, although experiments have been made in the forging alloys containing 2-4 percent copper. The Aluminum Manufactures, Inc., Cleveland, Ohio, and elsewhere, is reported to use an alloy containing 2.75-3.25 percent copper for forgings, but no details are available. When forged, such an alloy will give the following tensile properties: ultimate strength, 24,000 pounds per square inch; yield point, 16,000-17,000 pounds per square inch; and elongation, about 3.5-4 percent in a two-inch length.

### *Aluminum-Copper Rolling Alloys*

Light alloys of aluminum and copper, containing up to 11 percent copper have been hot rolled in an experimental way, but no commercial production of sheets or shapes has been made in these alloys. The limit of workability of the light aluminum-copper alloys was placed formerly at about 6 percent copper, but Schirmeister[26] has rolled them hot up to 11 percent. The most suitable composition, according to Schirmeister, is about 4 percent. All the alloys may be rolled hot at about 400°-450° C., but only the alloys low in copper (up to 4 percent) may be rolled cold, and then only by frequent annealing between passes. The physical properties of rolled aluminum-copper alloys, according to Schirmeister, vary with the composition as shown in Table III. Alloys of composition intermediate between those shown in the table have properties falling between the values given and fairly proportional to the copper content. In a rolled alloy, the effect of increasing the copper is to increase the hardness and ultimate strength and to decrease the elongation.

[26] Schirmeister, H., Zur Kenntnis der binaren Aluminiumlegierungen, Stahl u. Eisen, 1915, **35**, 649-652; 873-877; 996-1,000.

Alloys containing up to about 6 percent copper have been studied as regards their behavior in rolling by Carpenter and Edwards;[27] plates and sheets of various thicknesses were rolled. The ultimate strength which may be obtained by cold rolling, with anneals between passes and without cracking, ranges up to about 40,000 pounds per square inch, in these alloys for sheet, with an elongation of 4 percent on a three-inch length. Rolled light aluminum-copper alloys, say one containing about 4 percent copper, might be used instead of substantially pure aluminum for several purposes, and they might be advantageous because of their superior physical properties. These alloys would not be so good

TABLE III.

*Physical Properties of Rolled and Annealed Aluminum-Copper Alloys.**

| Composition, Elements, Percent | | Ultimate Strength, Pounds Per Square Inch | Elongation, on a 2-inch length, Percent | Brinell Hardness Number† |
|---|---|---|---|---|
| Al | Cu | | | |
| 99.0 | 1.0 | 21,000 | 26.0 | 41 |
| 94.9 | 5.1 | 25,300 | 21.0 | 49 |
| 89.0 | 11.0 | 27,700 | 16.0 | .. |

* Based on Schirmeister.

† Brinell hardness, 2.5 mm. ball under 62.5 kg.

as duralumin, but they might be suited better for some purposes, in the rolled condition, than either aluminum or 1.5 percent manganese-aluminum alloy.

GENERAL PROPERTIES OF THE LIGHT ALUMINUM-COPPER ALLOYS.

The principal report of investigations of the mechanical and other properties of the aluminum-copper alloys is that by Carpenter and Edwards.[28] In addition to extensive tests of the alloys rich in aluminum and rich in copper in the cast and worked condition, the constitution and equilibria of the system were studied also in this investigation. In the case of the cast alloys, compositions at either end of the series and some intermediate alloys were investigated, while the properties of certain of the alloys in the

[27] Carpenter, H. C. H., and Edwards, C. A., On the properties of the alloys of aluminum and copper; eighth report to the alloys research committee, Proc. Inst. of Mech. Engrs., 1907, 72, 57-269.

[28] Carpenter, H. C. H., and Edwards, C. A., *Loc. cit.*

form of hot-rolled and cold-drawn bars (with and without heat treatment), sheets, and plates were examined also. The report by Carpenter and Edwards represents the most complete one ever made on the aluminum-copper alloys, and, in fact, it serves as the only available text. The main conclusions arrived at will be indicated briefly here, together with some of the properties of

TABLE IV.

*Properties of Commercial 92:8 Al-Cu Alloy, as Determined by Three Laboratories.*

| List of Properties | | Reported by | | |
|---|---|---|---|---|
| | | Westinghouse Electric and Manufacturing Co. | Bureau of Mines | Lumen Bearing Co. |
| Ultimate strength pounds per square inch | Chill cast | ..... | ..... | 20,000-24,000 |
| | Sand cast | 19,800 | ..... | 16,000-20,000 |
| | Poured hot | ..... | 15,500 | ..... |
| | Poured cold | ..... | 20,000 | ..... |
| | at 260° C. | ..... | 19,300 | ..... |
| Yield point, pounds per sq. in. | | 15,400 | ..... | ..... |
| Elastic limit, pounds per sq. in. | | 5,000 | 13,000 | ..... |
| Elongation on a 2-in. length, percent | | 0.8 | 1.5 | 1.0—2.0 |
| Reduction in area, percent | | 4.9 | ..... | ..... |
| Transverse deflection, inches | | ..... | 0.22 | ..... |
| Transverse strength, lb. per sq. in. | | ..... | 290 | ..... |
| Impact resistance, blows | 4.7-lb. hammer | 300 | ..... | ..... |
| | 2.3-lb. hammer | 7,000 | ..... | ..... |
| Brinell hardness | | 50 | ..... | ..... |
| Specific gravity | | 2.83 | 2.84 | 2.80 |
| Shrinkage in 12x1x1 in. bars, inch | | 0.175 | ..... | $\frac{3}{16}$ in. per ft. |
| Coefficient of expansion, per ° C., 0°-100° | | 0.000024 | ..... | ..... |
| Resistance, microhms per cubic inch. | | 1.609 | ..... | ..... |
| Conductivity, percent | | 39.0 | ..... | ..... |
| Machining qualities | | ..... | soft and gummy | ..... |
| Hot-shortness values | At 705° C | ..... | 235 | ..... |
| | At 815° C | ..... | 90 | ..... |

the alloys. The general properties of the aluminum-copper alloys that are of interest to the foundryman and engineer include the following: behavior in the tensile test, specific gravity, casting and working qualities, resistance to corrosion, etc. Other properties are of especial interest in certain classes of engineering work. In Table IV, there are given the properties of commercial No. 12 alloy as determined[29] by three laboratories. The effect of pouring

[29] Anon., Results of tests of sand-cast metals and alloys, The Foundry, 1917, **45**, 271-273.

temperatures upon the properties of aluminum-copper alloys is of interest in foundry practice. The behavior of the alloys under the many usual mechanical tests applied to steel has not yet been studied in a detailed way, and some of the important physical properties have not been determined. Some of the more familiar properties which are of interest and importance are discussed below.

### *Specific Gravity.*

The specific gravity of the binary aluminum-copper alloys varies, of course, with the composition, and also with the condition,

TABLE V.

*Specific Gravity of Some Aluminum-Copper Alloys.**

| Composition, Elements Percent | | Condition of the Alloys | | | |
|---|---|---|---|---|---|
| Al | Cu | Sand Cast | Chill Cast | Rolled Bars | Drawn Bars |
| 99.14 | 0.86 | 2.72 | 2.73 | 2.73 | 2.73 |
| 98.10 | 1.90 | 2.73 | 2.75 | 2.75 | 2.75 |
| 97.23 | 2.77 | 2.75 | 2.77 | 2.77 | 2.77 |
| 96.34 | 3.76 | 2.77 | 2.79 | 2.79 | 2.79 |
| 95.03 | 4.97 | 2.78 | 2.81 | 2.81 | ... |
| 93.85 | 6.15 | 2.81 | 2.83 | 2.83 | ... |
| 93.09 | 6.91 | 2.82 | 2.85 | 2.85 | ... |
| 91.92 | 8.08 | 2.85 | 2.88 | 2.88 | ... |

* Based on Carpenter and Edwards.

*i. e.,* whether cast or worked. With the addition of copper to aluminum, the specific gravity rises regularly; the specific gravities of chill castings and drawn and rolled bars is identical. The specific gravities of sand castings are lower than those of chill castings of corresponding compositions, and in the former the values are likely to be erratic because of porosity. Values for some alloys in different forms are given in Table V. In the case of binary alloys of any two metals, the specific gravity may be calculated from the formula.

$$M = \frac{(W + w)Dd}{Dw + dW}$$

where $M$ is the mean specific gravity, $W$ and $w$ are the weights of the constituent metals, and $D$ and $d$ are their respective specific gravities. The actual specific gravity may not be the same as the

theoretical because of impurities, mechanical treatment, pouring temperature, rate of cooling and other factors. By calculation, the specific gravity of the 92:8 Al-Cu alloy is 2.859, and it happens that the theoretical value is practically the same as the actual value for this alloy in the cast condition.

Not many data are available as to the density of light aluminum alloys in the liquid state, but this is of much importance to both

TABLE VI.

*Density of Some Aluminum-Copper Alloys Over a Temperature Range.**

| Temperature | Condition of Alloy | Density | | | |
|---|---|---|---|---|---|
| | | Cu, 0.0 Percent | Cu, 7.84 Percent | Cu, 30.0 Percent | Cu, 59.9 Percent |
| **Centigrade temperature scale.** | | | | | |
| 20 | Solid | 2.706 | 2.857 | 3.433 | 4.680 |
| 700 | Liquid | 2,373 | 2.524 | 3.068 | 4.345 |
| 800 | Liquid | 2.345 | 2.494 | 3.032 | 4.300 |
| 900 | Liquid | 2.318 | 2.464 | 2.997 | 4.254 |
| 1,000 | Liquid | 2.291 | 2.434 | 2.962 | 4.208 |
| **Fahrenheit temperature scale.** | | | | | |
| 68 | Solid | 2.706 | 2.857 | 3.433 | 4.680 |
| 1,300 | Liquid | 2.371 | 2.523 | 3.066 | 4.344 |
| 1,400 | Liquid | 2.356 | 2.506 | 3.047 | 4.318 |
| 1,500 | Liquid | 2.341 | 2.490 | 3.027 | 4.293 |
| 1,600 | Liquid | 2.326 | 2.473 | 3.007 | 4.267 |
| 1,700 | Liquid | 2.311 | 2.456 | 2.988 | 4.242 |
| 1,800 | Liquid | 2.296 | 2.440 | 2.968 | 4.217 |
| 1,900 | Liquid | 2.280 | 2.424 | 2.949 | 4.192 |
| 2,000 | Liquid | 2.265 | 2.408 | 2.930 | 4.167 |

* Based on Edwards.

founders and die-casting makers. The density of some aluminum-copper alloys in the liquid state has been determined recently by Edwards.[30]

Table VI gives the density of some aluminum-copper alloys over a temperature range in the liquid state, as determined by the densimeter method. While there is no direct relationship between the density and chemical composition in this series of alloys, the specific volume, *i. e.*, the reciprocal of the specific gravity, is a linear function (nearly) of the composition over a considerable range.

[30] Edwards, J. D., Mechanism of solidification of a copper-aluminum alloy, Chem. and Met. Eng., 1921, **24**, 217-220.

### *Tensile Properties*

The tensile properties of some aluminum-copper alloys have been investigated by Carpenter and Edwards,[31] by Curry and Woods,[32] and many tests have been made in government and other laboratories. With regard to sand-cast light aluminum-copper alloys, the ultimate strength increases with increasing copper at the expense of the elongation, and with more than about 8 percent copper, the elongation is less than 1 percent—the alloys are quite brittle. With 11 percent copper, the ultimate strength of sand-cast bars is 20,000-21,000 pounds per square inch, and the elongation is practically *nil*. The ultimate strength varies from about 14,000 pounds per square inch to 22,500 pounds for alloys containing from 2 to 12 percent copper, respectively; in the same alloys, the elongation is about 6 percent to *nil*, respectively. Chill castings are stronger and usually more ductile than sand castings. Unfortunately, Carpenter and Edwards are in error as to some of the values they give for the ultimate strength of sand-cast alloys because they did not take account of their pouring temperatures. The figures given above refer to alloys poured at low temperature—about 670° C.

In actual castings, the strength will vary greatly from section to section, and a test bar cast coupon or separately will not show the strength of the casting at all points.

In the hot-rolled condition, the ultimate strength of the alloys increases up to about 6 percent copper and then commences to decrease, according to Carpenter and Edwards, while the elongation steadily diminishes. The strength of smaller hot-rolled sections is greater than that of larger ones, as might be expected. The ultimate strength of hot-rolled bars, 1.25-inch diameter, varies from about 20,000 pounds to 37,000 pounds per square inch for alloys containing from 1 to 6 percent copper, respectively; the elongation varies from 30 to 18 percent. Similarly, the strength of hot-rolled bars, 0.8125-inch diameter, varies from 28.5 to 15.5 percent. For cold-drawn bars, the ultimate strength may vary from 29,000 pounds to 45,000 pounds per square inch, for alloys containing from 1 to 4 percent copper, respectively; the

[31] Carpenter, H. C. H., and Edwards, C. A., *op. cit.*

[32] Curry, B. E., and Woods, S. H., The tensile strengths of the copper-aluminum alloys, Jour. Phys. Chem., 1907, **11**, 461-491.

elongation varies from 14.5 to 6 percent. The figures in Table VII give comparative values for a light aluminum-copper alloy, containing 3.76 percent copper, in various forms. The beneficial effects of mechanical work are shown by the figures in this table. From 0 to 8 percent copper, the alloys roll well, and from 0 to 4 percent copper, they draw sound.

In the case of plates and sheets, the strength obtainable, as in bars and rods, depends upon the amount of mechanical work. Values up to about 41,000 pounds per square inch are obtainable

TABLE VII.

*Physical Properties of an Aluminum-Copper Alloy, Containing 3.76 Percent Copper.**

| Physical Form | Yield Point, Pounds per Square Inch | Ultimate Strength, Pounds per Square Inch | Reduction in Area, Percent | Elongation on a 2-inch Length, Percent | Elastic Ratio |
|---|---|---|---|---|---|
| Chill cast ..... | 12,100 | 20,500 | 21.46 | 10.5 | 0.56 |
| 1.25-in. diameter rolled bar | 19,160 | 37,700 | 38.21 | 20.0 | 0.54 |
| 0.8125-in. diameter rolled bar.. | 26,000 | 38,100 | 49.76 | 21.0 | 0.68 |
| 0.8125-in. bar, drawn with annealing ..... | 34,700 | 37,900 | 21.79 | 8.0 | 0.92 |
| 0.90625-in. bar, drawn without annealing ..... | 41,400 | 44,800 | 20.84 | 7.5 | 0.92 |

* Based on Carpenter and Edwards.

by cold rolling, with anneals between passes, for an alloy containing about 4 percent copper. Broadly speaking, the alloy containing 4 percent copper is the most suitable one of the series at the aluminum end for working, yielding the best physical values.

Referring here briefly to the question of strength in a cast crankcase made in the 92:8 Al-Cu alloy, Skillman has discussed this, indicating that the strength varies[33] enormously in the different sections of the casting. Thus, coupon bars attached to such a casting, when made in the form recommended by the Society of Automotive Engineers, will have an ultimate strength

[33] Skillman, V., The non-ferrous alloy test-specimen question, Trans. Am. Inst. of Metals, 1913, **7**, 360-369.

of 18,000-20,000 pounds per square inch, when the alloy is poured at about 730° C. If such a crankcase is then dissected and the strengths of the various portions are determined, it will be found that the ultimate strength of the side walls, $\frac{3}{16}$-$\frac{1}{4}$ inch thick, might vary from 12,000 pounds to 20,000 pounds per square inch. The former value might be obtained for a section cut close to a large boss or lug, and the latter figure for a section under, or close to, a chill. The greater part of the side wall would yield figures from 15,000 pounds to 17,000 pounds per square inch. A piece cut from a bracket or brace, about 0.5-inch thick, would have a strength of only 12,000-13,000 pounds per square inch, while other sections of about the same thickness, but so located that they were more slowly cooled, would yield only 7,000-10,000 pounds per square inch.

The form of the specimen used for tensile tests of light aluminum-copper alloys, and for other aluminum alloys, is very important, and, while this matter cannot be dealt with here, it is advisable to point out that the form of specimen used should be given invariably when reporting tensile tests.

### *Pouring Temperature.*

Like most light aluminum alloys, the aluminum-copper alloys are quite susceptible to pouring temperature as regards strength, although some other alloys are much more susceptible to this factor. Gillett[34] has shown that the aluminum-copper alloys are about 20 percent weaker when poured hot than when poured cold, in compositions from 2 to 12 percent copper. The ultimate strength is affected, of course, by the size of section and the composition of the mold. On the basis of the tests by Gillett, the values given in Table VIII may be expected in sand-cast test bars poured at high and low temperatures. Unfortunately, many of the results reported in the literature for the ultimate strength of cast aluminum-copper alloys cannot be regarded as of value because no cognizance was taken of the pouring temperature. This factor also affects the soundness of cast alloys, as has been shown by the writer in another place,[35] and in actual practice close

[34] Gillett, H. W., The influence of pouring temperature on aluminum alloys, Eighth Intern. Cong. App. Chem., 1912, 2, 105-112.

[35] Anderson, R. J., Blowholes, porosity, and unsoundness in aluminum-alloy castings, Bureau of Mines Tech. paper 241, December, 1919.

pyrometric control is employed in the more modern and progressive foundries.

*Corrosion.*

Speaking broadly, the light aluminum-copper alloys are corroded strongly by sea water, but slowly by fresh water. They are, however, generally susceptible to the usual corrosion influences. In salt water, the rate of corrosion appears to increase

TABLE VIII.

*Effect of Pouring Temperature Upon the Strength of Aluminum-Copper Alloys.**

| Approximate Composition Elements Percent | | Low Pouring Temperature | | High Pouring Temperature | |
|---|---|---|---|---|---|
| Al | Cu | Pouring Temperature °C | Ultimate Strength Pounds per Square Inch | Pouring Temperature °C | Ultimate Strength Pounds per Square Inch |
| 98 | 2 | 663 | 13,800 | 843 | 11,500 |
| 96 | 4 | 663 | 15,500 | 843 | 13,000 |
| 94 | 6 | 663 | 17,600 | 843 | 14,500 |
| 92 | 8 | 663 | 20,000 | 843 | 15,500 |
| 90 | 10 | 663 | 21,000 | 843 | 16,000 |
| 88 | 12 | 663 | 22,500 | 843 | 17,500 |

* Based on Gillett.

with increasing copper content up to 2 percent and then to decrease with increasing copper above that content. Comprehensive tests on a series of the alloys, within the commercial limits as to composition, in a number of solutions including sodium hydroxide, sodium sulphate, sodium nitrate, sodium chloride, sodium carbonate, sodium acetate, and an alkaline tartrate have been carried out by Rowland.[36]

The corrosion of some light aluminum-copper alloys containing up to 6 percent copper, in fresh water and in sea water, has been examined by Carpenter and Edwards.[37] According to these

[36] Rowand, W. R., The electrolytic corrosion of the copper-aluminum alloys, Jour. Phys. Chem., 1908, **12**, 180-206.

[37] Carpenter, H. C. H., and Edwards, C. A., On the properties of the alloys of aluminum and copper; eighth report to the alloys research committee, Proc. Inst. of Mech. Engrs., 1907, **72**, 254-257.

investigators, the corrosion is strong in sea water, and the loss in weight diminishes with increasing copper above 2 percent; in fresh water, the alloys are practically uncorroded. In the former, aluminum hydrate is readily dislodged on shaking, but in the latter it remains as an adherent deposit which appears to prevent further corrosion. The question of the corrosion of the light aluminum-copper alloys under various conditions of service has not yet been thoroughly investigated, although numerous isolated tests of particular compositions have been made under many conditions. In alloy-development work, it would be of the greatest interest to obtain data with regard to the effect of various additive elements, in small percentages, upon the corrosion of the usual light aluminum-copper alloys.

## MODE OF MANUFACTURE.

In taking up the mode of manufacture of aluminum-copper alloys here, the methods used for the preparation of the light alloys are dealt with in this section of the paper, while the methods employed in the manufacture of intermediate alloys and of aluminum bronzes are taken up under Intermediate Aluminum-Copper Alloys and under Aluminum Bronzes in subsequent sections. Light aluminum-copper alloys for sand casting are made up, in the foundry, usually by melting together aluminum and an intermediate aluminum-copper alloy such as 50:50 Cu-Al. Or, they may be made by adding solid scrap copper to liquid aluminum. The present practice is not thoroughly standardized, as has been pointed out by the writer elsewhere.[38; 39] For casting purposes, primary No. 12 alloy pig is marketed directly to foundries by aluminum producers; this is manufactured simply by making a fixed addition of copper to aluminum by suitable means during a melting operation. In the same way secondary No. 12 alloy pig is marketed to foundries by secondary smelters and refiners. Such secondary pig may be made either by the direct smelting of No. 12 alloy scrap and borings, the resultant melt being pigged, or by melting aluminum scrap and making a fixed addition of copper.

[38] Anderson, R. J., Foundry methods for light aluminum-copper alloys, Chem. and Met. Eng., 1920, 23, 735-737.

[39] Anderson, R. J., Experiments in manufacturing No. 12 alloy, Chem. and Met. Eng., 1920, 23, 883-887.

An intermediate alloy, like 50:50 Cu-Al, is a very great convenience for use in making fixed additions of copper to aluminum. The alloy is brittle and can be readily broken into small pieces, and it is therefore easy to weigh out charges accurately. Copper, as such, is used because it will alloy satisfactorily[40, 41] under the proper conditions, and because, in some cases at least, it will be cheaper since it saves the cost of first making up an intermediate alloy. There is, however, difficulty, at times, in obtaining supplies of scrap and fine copper, owing to local and periodic metal market conditions, and in the majority of the larger foundries it is standard practice to employ the alloy containing about 50 percent copper and 50 percent aluminum for making fixed additions. The technical distinction between the various methods employed in the manufacture of light aluminum-copper alloys will not be taken up here, but it is of importance to know that the method to be used depends upon definite factors,[42] and these may be determined readily in a given foundry.

For sand casting, the light aluminum-copper alloys are melted in various kinds of furnaces, including pit furnaces using a crucible, in stationary and tilting crucible furnaces, in stationary and tilting iron-pot furnaces, in open-flame tilting furnaces, in reverberatories, and in electric furnaces. Casting temperatures in foundry work may be from 650 to 800° C., depending upon the type of casting poured.

The raw materials for the manufacture of commercial light aluminum-copper alloys may consist of aluminum, 50:50 Cu-Al alloy (or copper), foundry scrap including gates, risers, and defective castings, scrap castings from outside sources, aluminum-copper-alloy pig, etc.

While aluminum-alloy foundry practice cannot be taken up here at all, it is of importance to direct attention to a few of the more important technical problems involved in melting and molding. With regard to melting practice, it has been shown by the writer[43]

[40] Anderson, R. J., Some theoretical principles of alloying, Chem. and Met. Eng., 1920, **23**, 317-320.

[41] Anderson, R. J., Diffusion of solid copper in liquid aluminum, Chem. and Met. Eng., 1920, **23**, 575-577.

[42] Anderson, R. J., Foundry methods for light aluminum-copper alloys, Chem. and Met. Eng., 1920, **23**, 735-737.

[43] Anderson, R. J., Losses in aluminum and aluminum-alloy melting, Bureau of Mines Reports of Investigations, April, 1921, Serial No. 2239.

that the losses involved in melting the light aluminum alloys in foundry practice in the United States are exceedingly serious, and that furnace efficiencies are uniformly low. One of the most important problems before the aluminum industry today is the design of a melting furnace which will operate with low metal oxidation losses and high fuel efficiency—and at the same time at low cost and operating upkeep. Certain scientific problems attach to the solution of the difficulties which arise in melting practice, notably the effects of various gases at different temperatures upon aluminum alloys, and certain of these problems have been investigated in a preliminary way by the Bureau of Mines or are under survey. Thus, the question of the constitution of the atmospheres in contact with melting metal in aluminum-alloy furnaces has been studied by the writer[44, 45], and J. H. Capps in connection with a general study of melting aluminum alloys.

Referring now to the actual production of castings and to molding practice, it has been shown by an investigation of the Bureau of Mines, that casting losses, owing to foundry difficulties, are quite serious[46], but that the average losses may be reduced substantially by the exercise of certain precautions.

## INTERMEDIATE ALUMINUM-COPPER ALLOYS.

The intermediate alloys employed for introducing copper into aluminum in the production of light aluminum-copper alloys are those containing about 33 percent copper and 67 percent aluminum and 50 percent copper and 50 percent aluminum, respectively. These alloys are the socalled "rich alloys" or "hardeners" of foundry practice. The actual compositions employed are somewhat variable, and the 50:50 Cu-Al alloy is generally preferred. The mode of manufacture of intermediate alloys of this class has been discussed by the writer[47] in another place, and it is sufficient here to touch upon this matter only briefly. Ordinarily, the intermediate alloys are prepared by pouring liquid copper into liquid

[44] Anderson, R. J., and Capps, J. H., Gases in aluminum furnaces and their analysis, Chem. and Met. Eng., 1921, **24**, 1019-1021.

[45] Anderson, R. J., and Capps, J. H., Constitution of gas atmospheres in aluminum-alloy melting furnaces, Chem. and Met. Eng., 1921, **25**, 54-60.

[46] Anderson, R. J., Casting losses in aluminum foundry practice, Trans. Am. Foundrymen's Assoc., 1920, **29**, 459-487.

[47] Anderson, R. J., Manufacture of rich copper: aluminum alloys or hardeners, Chem. and Met. Eng., 1920, **23**, 617-621.

aluminum with stirring, and at the same time keeping the temperature as low as possible.

Both of the alloys mentioned above are brittle, but the 50:50 Cu-Al alloy is more brittle than the 33:67 Cu-Al alloy. The brittleness is owing to the presence of much $CuAl_2$. The former alloy melts at 575° C., and at the ordinary temperature it consists of the constituent *delta* ($CuAl_2$) plus eutectic. The 33:67 Cu-Al alloy has a lower melting point—540° C.—and is the eutectic alloy of the aluminum-copper series. It is less liable to segregation than the 50:50 Cu-Al alloy.

## ALUMINUM BRONZES.

Strictly speaking, the term aluminum bronze is a misnomer and the term has been used to describe a number of essentially different alloys. In engineering work, the term aluminum bronze is used to connote a copper-rich alloy of copper and aluminum, in which there may be present also iron, titanium, manganese, phosphorus, zinc, and other elements. Simple aluminum bronze is regarded generally as the alloy containing about 90 percent copper and 10 percent aluminum; a similar alloy containing iron may be called iron-aluminum bronze. Simple aluminum bronze, *i.e.*, 90:10 Cu-Al, has been employed more extensively than any other alloy in the aluminum bronze class, although, in more recent years, and especially in the United States, certain iron-aluminum bronzes have been growing in favor, *e. g.*, 89:10:1 Cu-Al-Fe. Aluminum bronze ranks with mild steel in tensile strength and ductility; it can be easily machined to a good finish; and it can be forged hot, as well as rolled into sheets. Sound castings can be made from it, but it normally gives considerable difficulty in sand casting practice because of shrinkage. Aluminum bronze has high resistance to corrosion by acids, sea water, and various atmospheres, and, in this respect, it is much superior to ordinary bronze and related copper-tin alloys.

The principal investigation of the mechanical and other properties of simple aluminum bronzes is the one carried out by Carpenter and Edwards[48], but extensive tests are due also to Tetmajer[49],

[48] Carpenter, H. C. H., and Edwards, C. A., On the properties of the alloys of aluminum and copper; eighth report to the alloys research committee, Proc. Inst. of Mech. Engrs., 1907, **72**, 57-269.

[49] Tetmajer, L., Methoden und Resultate der Untersuchung des Aluminiums und seiner Abkömmlinge, Mitteilungen der Material-sprufungs-Anstalt, Zurich, 1900, **9**.

and Curry and Woods[50], have determined the tensile strengths of the copper-aluminum alloys. More recently, studies of particular mechanical properties of some iron-aluminum, and other aluminum, bronzes have been made by Corse and Comstock.[51] One property of 10 percent aluminum bronze that is especially remark-

TABLE IX.

*Tensile Properties of Simple Aluminum Bronze, Containing 90.10 Percent Copper and 9.90 Percent Aluminum, in Various Forms.**

| Form and Condition | Yield, Point, Pounds per Square Inch | Ultimate Strength, Pounds per Square Inch | Elongation on a 2-inch Length, Percent | Reduction in area Percent |
|---|---|---|---|---|
| Sand casting ..... | 25,300 | 71,000 | 21.7 | .... |
| Sand casting, slowly cooled from 800°C. ..... | 29,800 | ..... | .... | .... |
| Sand casting, quenched from 800°C. ..... | 50,200 | 112,000 | 3.0 | .... |
| Chill casting ..... | 27,800 | 82,700 | 30.5 | .... |
| Chill casting, slowly cooled from 800°C. ..... | 37,000 | 59,100 | 5.0 | .... |
| Chill casting, quenched from 800°C. ..... | 39,600 | 86,400 | 22.0 | .... |
| Rolled bar, 1.25-in. diameter. | 30,500 | 78,500 | 31.5 | 30.52 |
| Rolled bar, 0.8125-in. diameter ..... | 33,200 | 85,300 | 28.8 | 30.80 |
| Rolled bar, 0.8125-in. diameter, slowly cooled from 800°C. ..... | 35,200 | 63,900 | 6.5 | 10.20 |
| Rolled bar, 0.8125-in. diameter, quenched from 800°C. | 58,700 | 101,900 | 11.0 | 16.78 |
| Cold-drawn bar, 0.8125-in. diameter ..... | 90,500 | 98,400 | 13.0 | 22.19 |

* Based on Carpenter and Edwards.

able, as first observed by Carpenter and Edwards, is the fact that the cast alloy has properties nearly equal to those in the rolled form.

The specific gravity of simple 10 percent aluminum bronze is about 7.55. The tensile properties of the various aluminum bronzes vary greatly depending upon the heat treatment, and

[50] Curry, B. E., and Woods, S. H., The tensile strengths of the copper-aluminum alloys, Jour. Phys. Chem., 1907, **11**, 461-491.

[51] Corse, W. M., and Comstock, G. F., Aluminum bronze: some recent tests and their significance, Proc. Am. Soc. for Test. Mats., 1916, **16**, part 2, 118-144.

Table IX will serve to give an idea of the properties of the alloy in various forms. The influence of the kind of casting, of mechanical work, and of heat treatment is shown by these figures. Under alternating stresses, the aluminum bronzes behave most remarkably, and in this respect they are as good as 0.45 per-cent. carbon steel.

Aluminum bronze is made usually by the addition of the requisite amount of solid aluminum to liquid copper, previously melted in a crucible.

Generally speaking, difficulty is had, in the case of alloys containing more than 10 percent aluminum, in obtaining a homogeneous alloy with a single melting, and a common practice for all aluminum bronzes calls for running the alloys into pigs, after preparation, and then subsequently using the prepared pigs for casting. Aluminum bronze may be used for a wide variety of engineering and construction purposes in place of phosphor bronze, so-called manganese bronze, and other bronzes and brasses where a high quality alloy, possessing superior physical properties is required. Owing to its relatively high acid-resisting and non-corrosive properties and its resistance to oxidation at a red heat, it is of especial value for particular purposes. Only a relatively small amount of aluminum bronze is used in the United States today, principally because of the difficulty experienced by the average foundry in sand casting it.

### USES OF ALUMINUM-COPPER ALLOYS.

Light aluminum-copper alloys are employed principally for sand castings in automotive work and also for die castings and permanent-mold castings. They have not been used to any extent for rolling or forging. Like any other alloys, whether steel or non-ferrous, the light aluminum-copper alloys cannot be regarded as suitable for all kinds of castings, although No. 12 alloy has been so used. They are, however, adaptable for many purposes, and within the range of composition of say 4 to 14 percent copper, alloys of greatly varying properties can be secured.

About 98 percent[52] of all the sand castings made in the United States are in light aluminum-copper alloys, and about 97 percent are in No. 12 alloy. No. 12 alloy is employed for crankcases, oil

[52] Anderson, R. J., Casting losses in aluminum foundry practice, Trans. Am. Foundrymen's Assoc., 1920, **29**, 459-487.

pans, various housings and cases, and other parts in automotive work, but for certain motor parts other aluminum-copper alloys are preferred. The alloy containing 9-10.5 percent copper is a favorite alloy for pistons, while the one containing 11-13.5 percent copper is used for manifolds. Cooking utensils, vacuum-cleaner parts, and a great variety of small miscellaneous castings are made in No. 12 alloy. In fact, this alloy is used for practically all kinds of castings, in contradistinction to some of the special alloys of simple and complex composition, which are employed for particular purposes, as, for example, certain aluminum-magnesium, aluminum-zinc, aluminum-copper-manganese, aluminum-copper-tin, and aluminum-copper-zinc alloys. Ordinary No. 12 alloy is reported to have been used for bearings[53] in railway work on the Northern Railway of France without showing any trace of wear after 50,000 miles, but in experiments with the same alloy on the Lancashire and Yorkshire Railway in England, considerable difficulty was experienced[54] in preventing heating under normal running conditions.

Patents pertaining to simple binary aluminum-copper alloys have been few, and, as is usually the case in alloys, inventors have appeared to prefer to deal with complex alloys. Gabriel[55], however, has patented an alloy containing small amounts of copper, citing 1.62 percent copper and remainder aluminum for working into tubes, plates, and wire. Very many ternary and complex alloys made by adding elements to aluminum-copper alloys have been patented, but these need not be taken up here.

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# RECENT DEVELOPMENTS IN ELECTRIC FURNACES OF THE MUFFLED ARC TYPE.[1]

By H. A. Winne[2].


## Abstract.

A description of muffled arc melting furnaces. Smaller units of 1500 pound and 100 pound per hour capacity are described in comparison to the larger rectangular shell type furnace. The advantages of muffled arc furnaces discussed are that little space for heating elements is required, metal losses by volatilization are reduced, a neutral or reducing atmosphere is maintained, and load fluctuations are small. They are adaptable to intermittent operation; other features are accessibility of hearth, low electrode consumption and small expense of refractories.

[A. D. S.]


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The advantages and economies of electrically melting brass, bronze, and similar non-ferrous alloys and metals, are so well known and have been so often discussed, that it is unnecessary to enumerate them here. It is the purpose of this paper briefly to describe some recent developments in the muffled arc type of non-ferrous metal melting furnaces, which it is believed represent a distinct advance in this field.

The rectangular shell type of muffled arc furnace illustrated in Fig. 1 is well known, and has been in successful commercial operation for some time. In this furnace a trench extends along each of two opposite sides of a rectangular hearth, separated from it by a carborundum bridge wall. A carbon cross electrode lies along the bottom of each trench, supporting on its upper surface

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two carbon "arcing blocks," one near each end. A vertical graphite electrode extends down through the roof above each arcing block, and the space in the trench around the cross electrode, arcing blocks, and the lower ends of the vertical electrodes, is filled with small pieces of broken graphite.

In operation, an alternating potential of about 60 volts is applied between the two vertical electrodes of each heating element, and current flows through the vertical electrodes, across very short arcs —practically contact resistances—between the electrodes and the

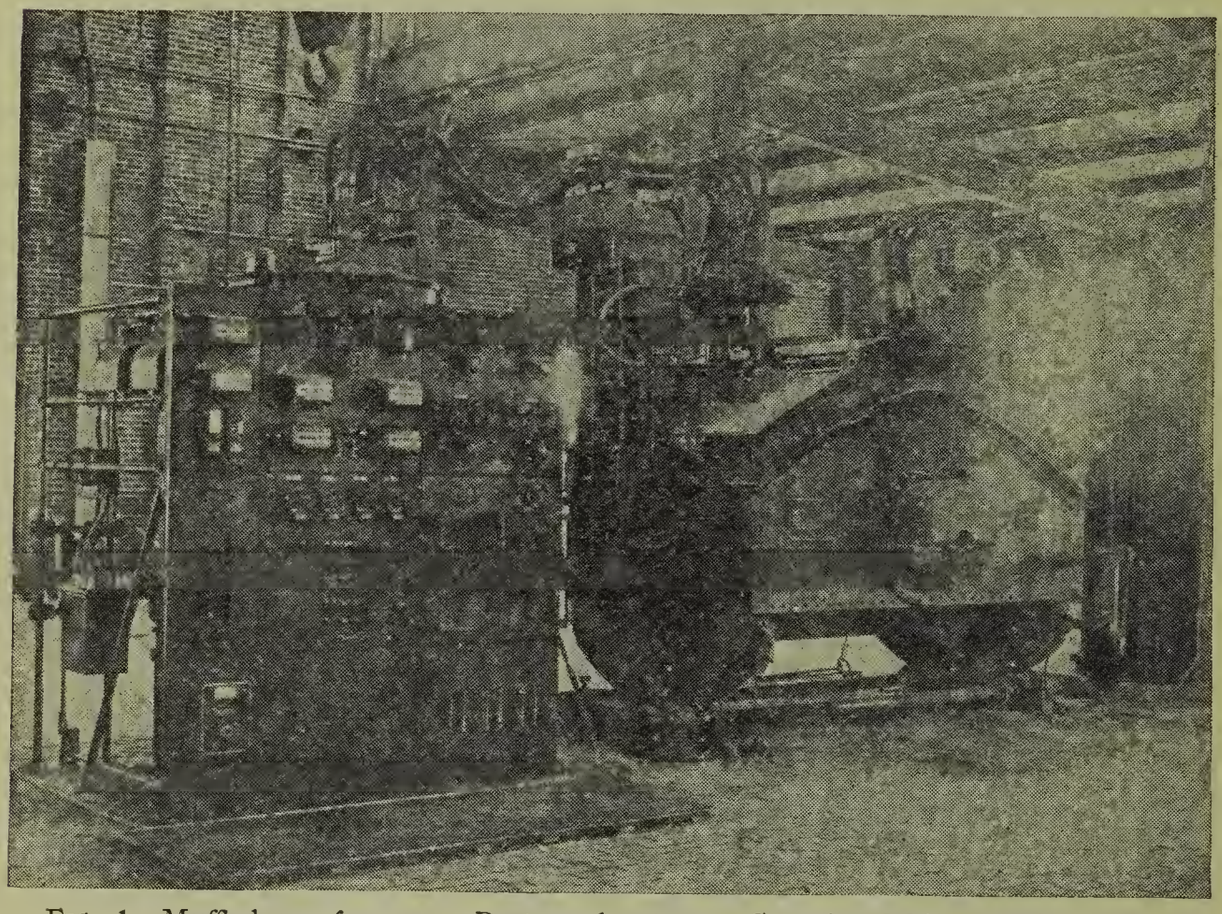

FIG. 1—Muffled arc furnace. Rectangular type. Capacity 2,250 pounds of brass per hour.

arcing blocks and broken graphite, and through the cross electrode and mass of broken graphite. Thus each heating element constitutes a single phase circuit, and, as there are two trenches, the furnace can be operated either as a single phase or a two-phase unit, and through three-phase to two-phase transformers will draw a balanced load from a three-phase circuit. The rate of power input is regulated by raising or lowering the electrodes, which are motor operated, and controlled by an automatic electrode regulator.

Heat is generated both by the flow of current through the

contact arcs, and through the cross electrodes and graphite. As the arcs are muffled or smothered in the broken graphite, this whole mass becomes heated throughout, and serves as a heat source of large area, and comparatively low, uniform temperature. Heat is conducted through the carborundum bridge walls to the

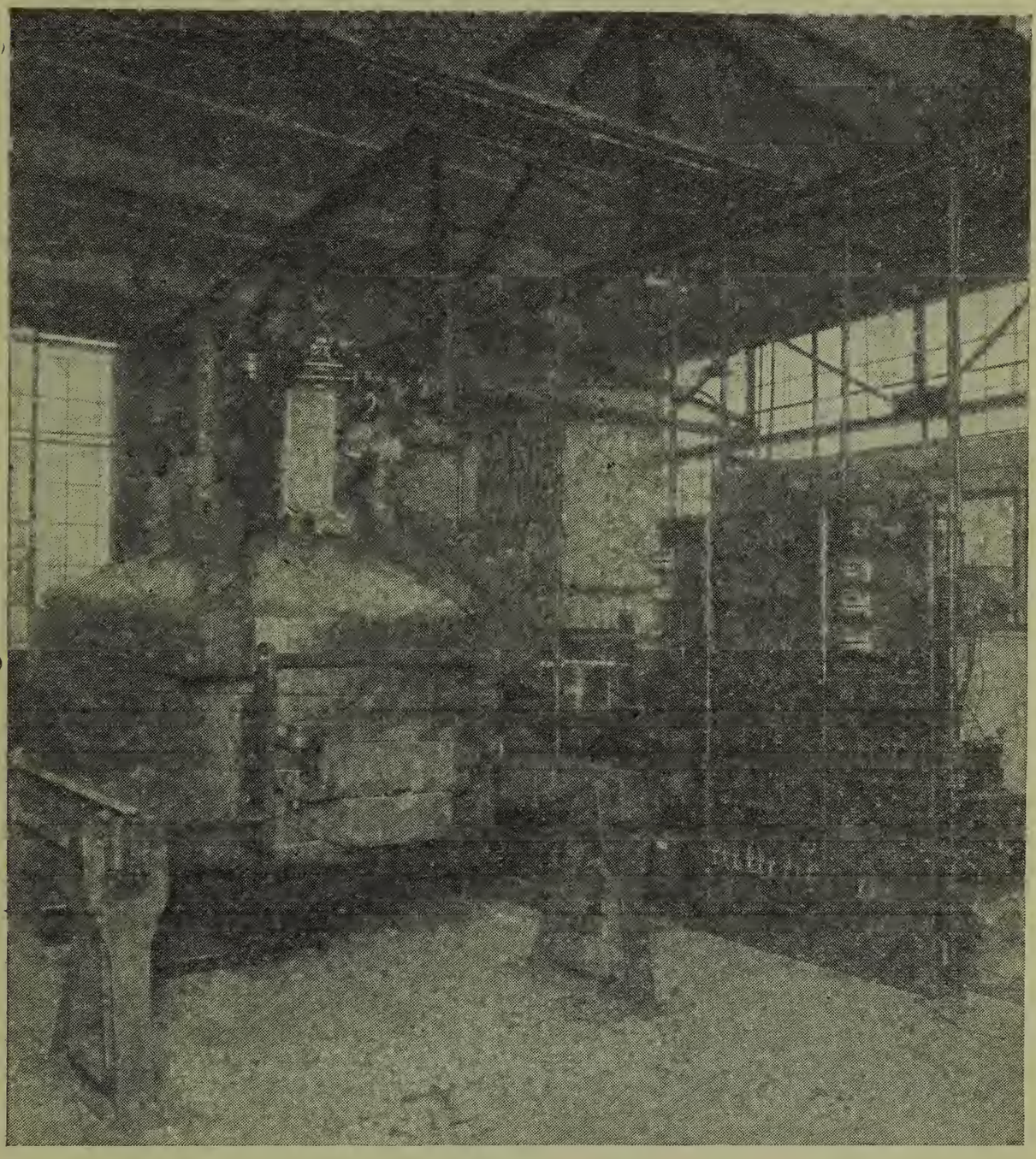

FIG. 2—Muffled arc furnace of new design. Capacity 1500 pounds of brass per hour.

metal in contact with them, and is also radiated to the roof, which is so proportioned and constructed as to reflect it to the metal on the hearth.

While, as previously stated, this furnace has operated very successfully, it is obvious that in this particular form the heating

trenches occupy a comparatively large space, and that in small capacities this rectangular unit would be unduly bulky, and might not be as efficient as desired. It was with a view to satisfactorily applying the advantages of muffled arc heating to furnaces of

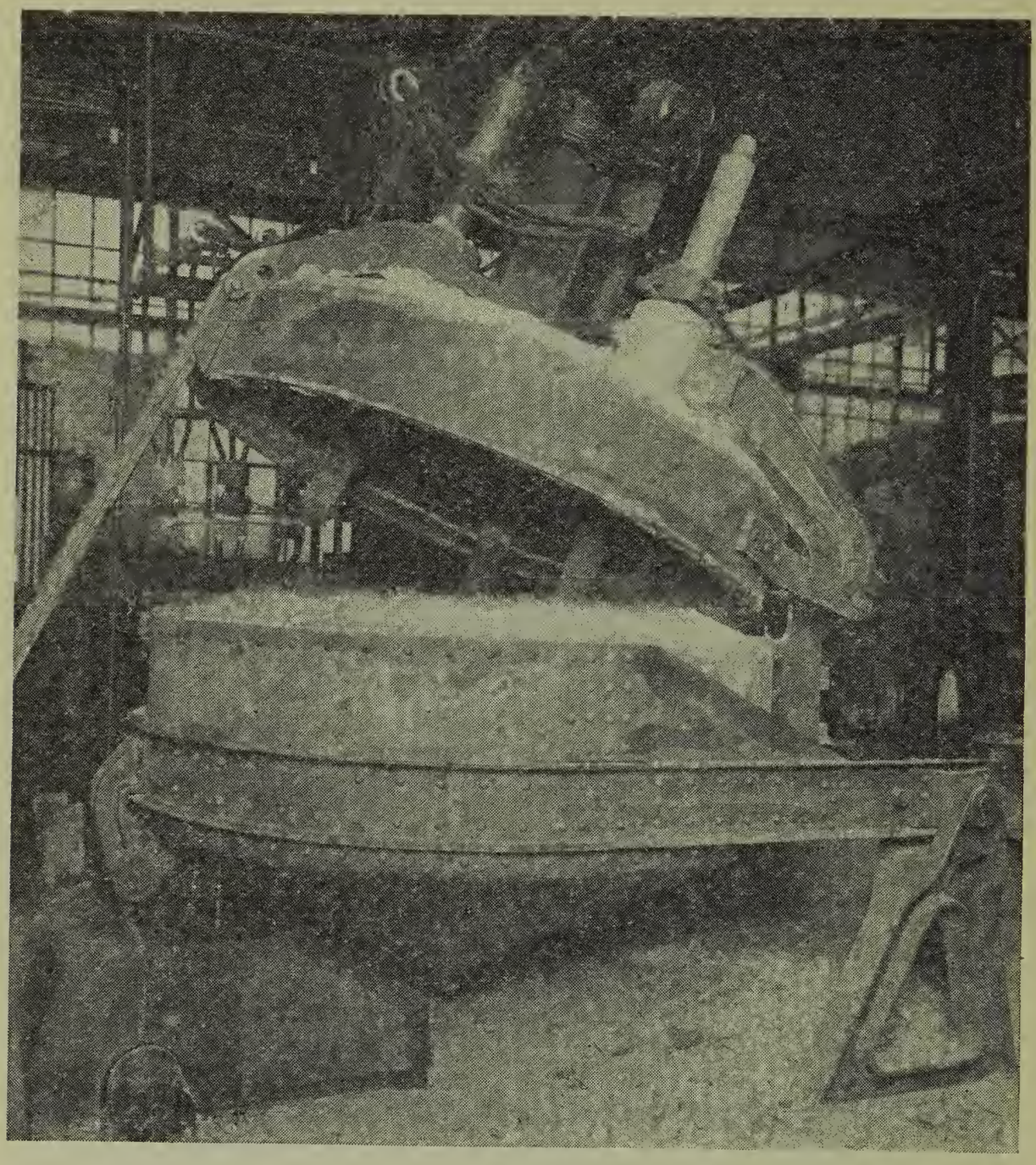

FIG. 3—Showing ease of lifting roof of muffled arc furnace for examination or repair of lining.

smaller capacity, that the furnaces about to be described were developed.

In the new design shown in Figs. 2 and 3, for units having a capacity of 1,500 pounds per hour or less, the furnace shell is cylindrical in horizontal section, with a bulged boiler head

bottom. It is lined with standard shapes of fire clay or other refractory, the arched roof being of the same material.

Three graphite cross electrodes lie between the first and third courses of brick in the bottom, radiating outward from the center to the side walls, spaced at angles of 120°. Their inner ends are embedded in a mixture of graphite and tar, which forms good electrical connection between them. On each cross electrode, at its outer end, is placed a large cylindrical carbon block, which is specially treated with a heavy coating of carborundum cement, making it highly resistant to oxidation at the temperatures to which it is subjected.

These blocks are adjacent to the side walls, to which they are cemented. They project a considerable distance above the furnace hearth, and their upper ends are hollowed out, saucer-shaped. Extending down through the roof above each of these blocks is a vertical graphite electrode. The spaces in the saucer-shaped depressions in the tops of the arcing blocks, around the lower ends of the graphite electrodes, are filled with broken graphite.

It is obvious that the cross electrodes connect the electrode circuits in Y, allowing three-phase power to be utilized in this furnace. In operation, the three vertical electrodes are connected to a three-phase, 60-volt circuit. Short arcs are drawn between the electrodes and the blocks and graphite. The heat generated by these arcs, as well as by the passage of current through the graphite, serves to heat the mass of graphite and the blocks to a high temperature. Heat is conducted from the blocks to the metal in contact with them, and also radiated from them to the metal; in addition, a certain amount is radiated to the roof and reflected to the charge.

The rate of power input to the furnace is regulated by raising or lowering the vertical electrodes. These electrodes are motor operated, and automatically controlled. A very small movement of the electrodes makes a large change in power input, consequently a very slow electrode speed is employed.

This type of furnace possesses many advantages. While the heating elements occupy very little space, still they are sufficiently large to give a great amount of surface for radiation and for contact with the metal. Consequently, the temperature gradient between the heating elements and the metal is maintained com-

paratively low, thus reducing the metal losses when melting volatile metals.

Another factor in reducing metal loss in all muffled arc furnaces is that, due to the presence of incandescent carbon, the furnace atmosphere is neutral or reducing, thus limiting oxidation.

As the power input is automatically regulated, the temperature can be easily controlled. Automatic electrode regulation also decreases the amount of attendance required.

Due to the excellent electrical characteristics of the muffled arc furnace it makes an especially desirable load for the central station or the small power plant. It operates as a steady balanced three-phase load, at a power factor of 95 percent or better, free from

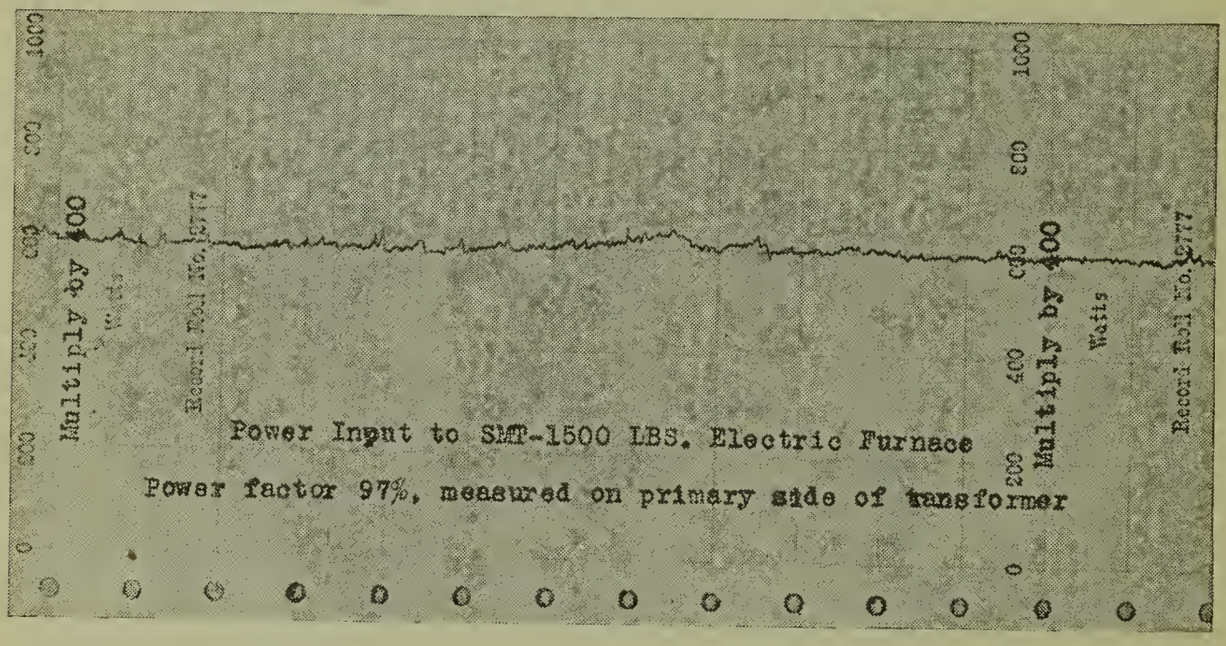
Power Input to SMT-1500 LBS. Electric Furnace
Power factor 97%, measured on primary side of transformer
Multiply by 100
Record Roll No. 2777
Watts

FIG. 4—Curve-drawing wattmeter record of power input to 1500 pound, 250 kw. muffled arc furnace.

the fluctuations usually incident to the operation of electric arc furnaces.

Power can be put into the furnace at a high rate, thus allowing it to be heated up quickly, an important consideration in intermittent operation.

The hearth is readily accessible at all times, and the metal can be stirred or skimmed as desired, without shutting off the power, or interfering with operations in any way.

One of the illustrations shows the ease with which the roof may be raised, for inspection or repair of the lining. No crane or hoist is required. The furnace is simply tilted forward by means of the tilting mechanism, a timber or other support placed from

the rear of the roof ring to the floor, and the shell tilted back to normal position. The roof ring, with the electrode support, is hinged to the shell at the front.

No cooling water is used on the electrode holders or on the roof where the electrodes pass through it. Specially designed holders, and a novel type of electrode sleeve on the roof, obviate the necessity for other than natural air cooling.

In practical operation, this furnace has given very satisfactory results. A unit capable of melting 1,500 pounds of brass per hour has been thoroughly tested and operated for several months. Equipped with a 250 kva., three-phase transformer, it will melt yellow brass, operating 24 hours per day, one heat per hour, with a power consumption of 250 to 300 kw. hours per ton. For nine-hour operation the power consumption is 325 to 375 kw. hours per ton, including the power required for warming the furnace up in the morning.

The metal loss in melting yellow brass is less than 1.5 percent. A careful record was kept of the weights of a number of successive heats of metal containing about 30 percent Zn, and the average total loss by weight, including spillings, etc., was only 1.14 percent.

The electrode consumption is low, averaging from 1.5 to 2.5 pounds per ton of metal melted, depending on how the furnace is operated. Only a small amount of broken graphite is used, approximately one pound per ton of metal. The graphite is easily replenished by means of a long handled spoon inserted through the charging door. This operation is required not more than once a day.

The expense for refractories on this furnace is small. The side walls immediately behind the electrodes have an inner course of carborundum brick, which gives them ample protection. The remainder of the lining is of standard fire clay shapes. After several months operation it shows very little sign of deterioration. For examination and repair of the lining, the roof can easily be lifted as previously noted.

The arcing blocks, coated with carborundum cement, have a very long life, needing only an occasional patching. The coating of cement has proven to be very hard, highly resistant to abrasion and oxidation, and adheres very firmly to the block. When the

experimental furnace was first constructed, instead of coating the blocks with cement they were enclosed in cylinders built up of carborundum brick. This construction was also very satis-

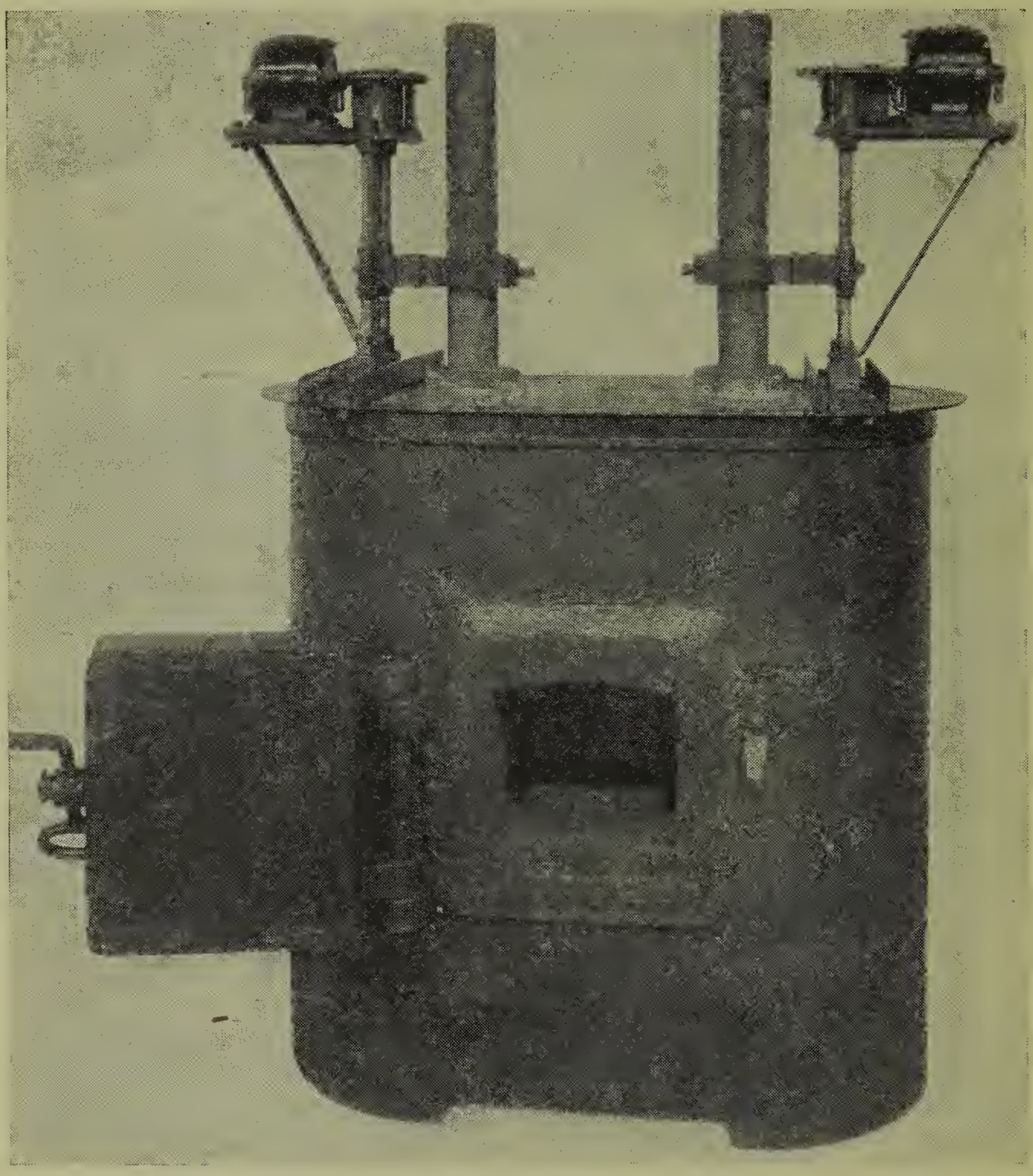

FIG. 5—Small muffled arc furnace. Taking standard No. 20 crucible.

factory from an operating standpoint, but of course the brick occupied more space than the coating of cement.

While, so far, this new type of muffled arc furnace has been tried out only in the plant of its manufacturer, the results obtained are so encouraging that it is believed it will prove a very satisfactory melting unit for the non-ferrous foundry.

To fill the demand for a small electric furnace, adaptable to

various processes, and capable of reaching a temperature of 1500° C. (2732° F.), there has recently been placed on the market the furnace illustrated in Fig. 5. This also is of the muffled arc type. Its hearth is flat, and level with the bottom of the door, arranged to receive a standard graphite melting crucible.

This furnace is a single phase unit and has the usual cross electrode, cylindrical carborundum coated arcing blocks, and vertical graphite electrodes. The vertical electrodes are operated by small alternating current motors, controlled by a remarkably simple and efficient automatic regulator. Power for the motors is drawn from the electrode circuit, so that no other supply circuit is necessary.

The furnace is lined with special shapes of fire clay, the main lining consisting of only four pieces, a bottom, a back, a front and a top. The hearth is of carborundum brick. The lining may easily be put in place by an ordinary workman, the services of a mason not being required. The lining life is long; one lining has been used through several months of tests and operation at 1200° C. to 1500° C., and is still in excellent condition. This may be considered somewhat remarkable in view of the comparatively small distance from the muffled arc to the lining.

The hearth and door of this small unit are designed to receive a standard No. 20 graphite crucible, which has a capacity of about 50 pounds of brass or copper. The furnace is equipped with a transformer of 40 kva. capacity, so that it will melt yellow brass at the rate of 100 to 125 pounds per hour, with a power consumption of 35 to 40 kw. hours per 100 pounds of metal melted, on the basis of continuous operation.

Except for the fact that it requires single phase power, this furnace possesses the operating advantages of the larger muffled arc units. Obviously, so small a furnace cannot readily be made as efficient as the larger unit. It is a very convenient piece of apparatus for the small foundry, the laboratory, the manufacturing jeweler, and the repair shop. Temperatures up to 1500° C. can be attained with ease. It is adaptable to various conditions, as by changing crucibles entirely different metals can be melted in succeeding heats without danger of contamination. By using two small crucibles, two different metals can be melted at the

same time. The furnace can also be used to heat metals for heat treating, or forging, and so should be especially valuable in small repair shops. It is adaptable to heat-treating high speed steel, a field which is beyond the temperature limitations of the metallic resistor furnaces.

The chief novel feature of the furnaces described in the foregoing is the substitution of the compact, cylindrical carborundum coated arcing block for the rectangular heating element, thus reducing the space required by the heating element, and allowing the many marked advantages of the muffled arc principle of heating to be applied efficiently to small units.

The field of the muffled arc melting furnaces embraces practically all metals requiring pouring temperatures of not over 1500° C. (2732° F.). This temperature seems to be about the upper limit at which a reasonable lining life can be obtained. Two of the rectangular type units have operated successfully for two years or more on a metal which is poured at temperatures from 1425° C. to 1525° C.

The furnaces are especially useful in melting alloys containing elements which volatilize at low temperatures, or are easily oxidizable. This is true because of the low temperature gradient between the heating element and the metal, and the neutral or reducing atmosphere in the furnace. They successfully melt all grades of brass and bronze, including turnings and borings, copper, aluminum, monel metal, and numerous other metals and alloys.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# ELECTRIC-FURNACE PURIFICATION OF ZIRKITE.[1]

By J. G. Thompson.[2]

Abstract.

The purpose of this investigation was to determine to what extent the impurities might be removed from zirkite ore in the electric furnace. In the resistance type furnace the rate of power input was insufficient to attain the high temperature (above 2220° C.) desired. In the arc type, 90-95 percent of silicon was removed from the ore; an amount of carbon added sufficient to transform only silicon to the carbide gave the best results. With excess carbon, a double carbide of silicon and zirconium probably forms which requires further study. [A. D. S.]

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The extreme stability at high temperatures of certain zirconium compounds, particularly the oxide and carbide, together with the fact that these compounds are not appreciably volatile below their points of decomposition, suggested the use of electric heating as a means of obtaining pure zirconium oxide from zirkite ore, by eliminating silicon, iron and titanium, whose oxides and carbides are presumably less refractory than those of zirconium. Hitherto the electric furnace[3] has been employed only as a preliminary step in the purification of zirkite, apparently for the purpose of decomposing the refractory silicates. This investigation was undertaken, therefore, for the sake of ascertaining to what extent zirkite (impure zirconium oxide) might be freed from impurities by direct heating in an electric furnace.

Owing to the great difficulty and tediousness of the analytical

[1] Manuscript received August 6, 1921.

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[3] Moissan: Comptes rend., 1893, **116**, 1222; Troost: *Ibid*, 1893, **116**, 1428; Weiss and Lehmann: Zeit. anorg. Chem., 1909, **65**, 178; Podszus: Zeit. angewandte Chem., 1917., **30**, 17; Barton: U. S. Pat., 1,342,084.

work necessary, it was decided to limit this study to the three impurities, iron, silicon and titanium. Two possibilities suggested themselves in regard to the elimination of silicon and iron, as follows:

1. Reduction of the oxides in the presence of an excess of iron, forming ferro-silicon which could be removed later by mechanical means.

2. Reduction of the oxides to the metals or carbides, which could be volatilized or decomposed subsequently by the application of high enough temperatures.

The first possibility was tested experimentally in an arc furnace without very promising results and was therefore abandoned early in favor of the second. It seemed difficult to obtain a melt fluid enough to permit the proper and necessary coalescence of the ferro-silicon, at any rate except at extremely high temperatures. And if such temperatures were necessary, it seemed best to eliminate the iron and silicon by direct volatilization.

Preliminary experiments conducted in a small arc furnace, indicated that zirconium carbide is stable at temperatures far above the decomposition point[4] of silicon carbide. This led to the belief that conversion of the entire ore to carbides, followed by exposure of the mixed carbides to temperatures greater than 2220° C., at which silicon carbide decomposes, would eliminate silicon and perhaps some or all of the iron and other impurities. It would then be possible to transform zirconium carbide to the oxide by heating in air and pure and highly refractory zirconia might therefore be obtained.

The zirconium ore employed in this investigation was a finely ground zirkite 65 percent of which passed through a 100 mesh sieve. Duplicate analyses of the ore showed the following ratio of elements:

100 Zr: 15.1 Si: 5.37 Fe: 0.89 Ti

The first series of experiments were carried out in a resistance furnace of the silicon carbide type[5], sufficient carbon being added to insure the transformation of the various oxides present into carbides. Later experiments were performed in an arc furnace, the amount of carbon being varied from run to run.

[4] Cf. Gillett: Jour. Phys. Chem., 1911, **15**, 213.
[5] Cf. Gillett: *loc. cit.*

## Part I.—Experiments with a Resistance Furnace.

The resistance furnace was built in the form of a rectangular trough 7 inches wide at the bottom, 8 inches wide at the top, 9 inches deep, and 29 inches long. The floor was built of zirkite bricks supported by a double layer of fire brick. The sides were built of fist-size lumps of zirkite, backed with fire brick, and faced smooth with ground zirkite bonded with a little water glass. The end walls were faced with zirkite brick which were backed up by fire brick. The sides and floors were permanent. The end walls were torn out after each run to facilitate removal of the charge. The electrodes were pieces of 4-inch square, carbon electrodes which entered through the center of the end walls and protruded four inches into the furnace. The outer ends of the electrodes were water-cooled and connected to bus bars by flexible leads. Power was supplied by a 75 kilowatt motor-generator set. 2000 amperes was the largest current available, representing the maximum output of the motor-generator set.

The complete conversion of 100 parts of ore to the various carbides and carbon monoxide, requires approximately 33 parts of carbon. To insure the presence of an excess of carbon, a ratio of 45 parts of carbon to 100 parts of ore was used. Petroleum coke, 10-20 mesh in fineness, supplied the carbon for most of the runs, although in one or two cases granular electrode carbon was tried.

Four runs were made in the resistance furnace. Since the runs were all more or less similar, the first one only will be described in detail, as follows:

*Run 1.*

| | |
|---|---|
| Ratio of ore to carbon in charge | 100 : 45 |
| Total weight of charge | 86.5 pounds |
| Core | a double line of graphite electrode pieces, one inch in diameter, the junctions packed in petroleum coke to insure contact. |
| Time of Run | 1 hour, 52 minutes |
| Power consumption | 60 K. W. H. |

The charge was packed loosely in the furnace up to the level of the electrodes. The core was inserted and the remaining charge added, filling the furnace. At first it required a poten-

tial of 46 volts to produce a current of 400 amperes through the furnace. Small gas volcanoes appeared almost at once, followed by flames, bright yellow at the base with reddish-yellow tips. The power input was maintained as high as possible, being limited by the violence of the gas evolution which resulted in loss of charge when the power input became too high. After the first violent evolution of gas subsided the charge presented the appearance of gentle boiling. After half an hour, when the total power input had reached 15 K.W.H., one end of the charge stopped boiling and settled to form a crust. This effect spread gradually until the entire charge was crusted over and quiet. Heating was continued about half an hour more. The entire charge finally became bright red in color but the temperature could not be raised further. At first the current was carried almost entirely by the core. However, the charge itself soon began to conduct with the result that the current rose and the voltage fell off rapidly, until at the end of the run the current reached 1750 amperes and the voltage dropped to 5. These results made it evident that the conductivity of the core and heated charge was too great to allow the input of power at a sufficient rate. On account of this circumstance, it proved impossible to reach the very high temperature desired.

When the cooled charge was examined, a grayish-black granular core about four inches in diameter was found in the center, extending the length of the charge between the electrodes. Small deposits of spongy material, metallic in appearance and rather bluish in color, which subsequent examination proved to be zirconium carbide, were found in close proximity to the original core. The total weight of sponge was about 6 pounds. The remaining contents of the furnace consisted of unchanged charge. The original graphite core was not attacked, indicating the presence of an adequate supply of carbon in the charge. Some slight indications of the volatilization of silica were found on the furnace walls, but the power input evidently was too low.

The three subsequent runs were made in an attempt to increase the power input, but without marked success. The yields of carbide "sponge" were 6.5, 10 and 7.5 pounds respectively. The carbide "sponge" was removed from the furnace in each run and analyzed. Owing to the complex nature of the analytical pro-

cedure the details have not been included in the present paper but will be described in detail in a later report. The results of the four runs may be summarized as follows:

TABLE I.

| Run | KWH | Av.kw. | Carbide "Sponge" Pounds | Metal Ratio in "Sponge" | | | |
|---|---|---|---|---|---|---|---|
| | | | | Zr | Si | Fe | Ti |
| 1 | 60 | 32 | 6.0 | 100 | 3.7 | 4.48 | 0.79 |
| 2 | 75 | 34 | 6.5 | 100 | 11.0 | 5.50 | 0.78 |
| 3 | 100 | 38 | 10.0 | 100 | 12.2 | 7.60 | 0.79 |
| 4 | 80 | 40 | 7.5 | 100 | 5.5 | 2.60 | 0.87 |
| | | | original ore | 100 | 15.1 | 5.37 | 0.89 |

The behavior of the carbide "sponge" on analysis showed that most of the silicon was present as the carbide, thus indicating that in general the temperature of the mass was not high enough to insure the removal of all the silicon by volatilization. As the data indicate, the removal of silicon varied in a very irregular manner, being fairly complete in some cases but very incomplete in others. Other samples from portions of the charge further removed from the core showed higher ratios of silicon to zirconium. This follows naturally, since volatilization of silicon would occur first in the hottest part of the charge, *i.e.*, around the core, and would be less evident in regions at a greater distance from the source of heat.

The data indicate little or no elimination of titanium or of iron, except in the fourth run, where much iron was apparently removed. In this run, however, about 9 pounds of common salt was added to the charge and this no doubt brought about volatilization of much of the iron as the chloride. All things considered, the results obtained with the resistance furnace were unsatisfactory and this type of furnace was abandoned in favor of one of the arc type.

## PART II.—EXPERIMENTS IN AN ARC FURNACE.

The furnace shell of the arc furnace consisted of an iron pot, lined with fist-sized pieces of zirkite ore, faced smooth with

ground zirkite bonded with a little water-glass. The zirkite facing and the charge proper contained the same ratio of carbon to zirkite. The resulting hearth was cone-shaped, 8 inches in diameter at the top, 4 inches in diameter at the bottom, and 8-10 inches deep. This lining was torn out after each run to facilitate removal of the charge. The lower, horizontal electrode, composed of two 2-inch square graphite electrodes, formed the floor of the hearth, entering through a rectangular opening in the side of the cast iron pot. The upper electrode was a 4-inch square carbon electrode, suspended in a vertical position and counterweighted to allow adjustment. Both electrodes were clamped in water-cooled electrode holders and connected to bus bars by means of flexible cables.

The first run performed in this furnace will be described in detail, as being typical of all the runs carried out subsequently.

*Run 5.*

| | |
|---|---|
| Ratio of ore to carbon in charge | 100 : 45 |
| Total weight of charge | 11 pounds |
| Time of run | 45 minutes |
| Power consumption | 32.5 K. W. H. |

The run was started by striking an arc between the bare electrodes. The walls of the cone began to slag down almost immediately. Accordingly, the first addition of charge was made as soon as possible after starting the arc. The charge was fed in slowly and was observed to solidify when it reached the zone of the arc. During the early stages of the run the arc was smothered by the charge. After all the charge had been added to the furnace, the arc was run open but remained fairly quiet. The current was maintained at about 1000 amperes until the evolution of fumes had almost ceased when the arc became noisy and hard to maintain. The run was stopped when this point was reached.

The top of the charge oxidized during cooling, forming a layer of fine white oxides, below which lay a brittle, black mass weighing approximately 3.5 pounds. A sample for analysis was taken from the center of this cake and gave the following ratio:

100 Zr : 4.85 Si : 6.38 Fe : 0.70 Ti

A series of runs was made in which the ratio of carbon (petroleum coke) to zirkite ore was varied systematically. The results are assembled in the following tables.

TABLE II.

*Effect of Varying Ratio of Ore to Carbon.*

| Run | Charge lb. | Ratio Ore to Carbon | KWH | Yield of Purified Product lb. | Metal Ratio in Product | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Zr | Si | Fe | Ti |
| 5 | 11.0 | 100 : 45 | 32.5 | 3.5 | 100 | 4.85 | 6.38 | 0.70 |
| 9 | 12.5 | 100 : 25 | 18.25 | 3.0 | 100 | 3.03 | 6.50 | 0.64 |
| 10 | 12.0 | 100 : 20 | 17.5 | 3.1 | 100 | 2.21 | 5.00 | 0.55 |
| 11 | 15.4 | 100 : 15 | 21.5 | 5.0 | 100 | 0.88 | 5.92 | 0.70 |
| 18 | 15.4 | 100 : 10 | 19.3 | 7.0 | 100 | 1.31 | 8.73 | 0.69 |
| 19 | 16.8 | 100 : 5 | 27.0 | 9.9 | 100 | 1.86 | 6.67 | 0.73 |
| | | | | Original ore | 100 | 15.70 | 5.37 | 0.89 |

TABLE III.

*Elimination of Impurities.*

| Run | Ratio Ore to Carbon | Percentage Elimination of: | | |
|---|---|---|---|---|
| | | Si | Fe | Ti |
| 5 | 100 : 45 | 68 | —19 | 21 |
| 9 | 100 : 25 | 80 | —21 | 28 |
| 10 | 100 : 20 | 85 | 7 | 38 |
| 11 | 100 : 15 | 94 | —10 | 21 |
| 18 | 100 : 10 | 91 | —62 | 22 |
| 19 | 100 : 5 | 88 | —24 | 18 |

So far as the elimination of silicon is concerned, the data show that the arc furnace gave more consistent results than the resistance furnace afforded. Some titanium was also eliminated but no iron, there being an apparent increase in the amount of the last impurity. Owing, however, to the difficulty of determining accurately the amount of iron, the apparent increase, especially in Run 18, may be due to an error in analysis. One may safely conclude, notwithstanding, that no iron was eliminated under the conditions of experiment.

The data obtained with the arc furnace show a maximum

in the removal of silicon when the ratio of zirkite to carbon is 100:15. Calculations based on the silica content of the ore showed that a little more than 10 parts of carbon to 100 of ore was just enough to transform all the silica into carbide (carborundum) and carbon monoxide. We have therefore come to the conclusion that the best high-temperature elimination of silicon is obtained when little more than enough carbon is used to form carbide with the silicon only, leaving the zirconium undecomposed as oxide.

When more than 15 parts of carbon were used the elimination of silicon became steadily less complete. Under these circumstances it is known that zirconium carbide is actually produced in the arc. The zirconium carbide therefore appears to retain some of the silicon and the suggestion is offered that stable double carbides of silicon and zirconium may be produced or that the two carbides form solid solutions or mixed crystals. Experiments to throw light upon this hypothesis are now under way in this laboratory.

Other runs were made in which sodium chloride was added to the charge of ore and coke to aid in the removal of iron, but curiously enough no iron was eliminated in this way. It is possible that the rapid attainment of the high temperature under the ore decomposed the chloride before it could be volatilized away.

Runs in which granular electrode carbon was substituted for petroleum coke showed that better results may be obtained on a small scale with the more finely divided coke.

An interesting fact brought out by these experiments is the high melting point and stability, in a reducing atmosphere, of the carbide of zirconium. As long as there was an excess of carbon present, over and above the amount required for the complete conversion of the oxides to carbides, it was impossible to melt the product even under the direct action of a 40-50 kilowatt arc.

The partially purified carbide apparently had a higher melting point than the oxide product with the same relative composition. This was shown in the runs in which the ore melted and formed a pool under the arc, the pool solidifying as soon as more carbon was added. In order to use the carbide as a refractory, however, it would be necessary to protect it from oxidation. The black

carbides all burned readily in the air to form light, fluffy oxides. Heating the powdered carbides to dull redness is sufficient to start the oxidation which then proceeds slowly but persistently.

A series of experiments was next carried out on the removal of iron by treatment of the carbides or mixed oxides and carbides with chlorine[6] at both low and high temperatures. The results indicated that iron may be removed in this way from zirconium carbide at low temperatures and, at high temperatures, from zirconium oxide from which silicon had been largely eliminated in the arc furnace. It would seem, therefore, that a fairly pure zirconia for refractory purposes might be made from crude zirkite ore by eliminating as much as possible of the silicon in an electric furnace and by following this by treatment with chlorine or phosgene[7] to remove the iron.

This investigation is admittedly incomplete in many ways. The limited time at our disposal and the difficulty of and the time consumed by the analytical work involved, may be offered as an excuse. It is hoped, however, that attention will be called to the problem of large-scale purification of zirconium oxide, so that the latter may become more generally available as a refractory material for very high temperatures. A summary of the results obtained follows:

1. 90-95 percent of the silicon may be largely removed from siliceous zirkite ore by heating a mixture of ore and carbon to a temperature greater than 2220° C. in an electric furnace.

2. The best results appear to be obtained by feeding into an arc furnace a mixture of ore and coke, the amount of carbon being approximately that required to transform only the silicon to the carbide.

3. The existence of stable double carbides of silicon and zirconium or of solutions of silicon carbide in solid zirconium carbide has been suggested as an explanation of the incomplete removal of silicon when carbon in excess of that required to form only silicon carbide is used.

4. It is suggested that zirconia sufficiently pure for refractory purposes might be obtained from zirkite ore by removing the

[6] Cf. Phillips: Jour. Amer. Ceramic Soc., 1918, **1**, 791.

[7] Cf. Baskerville: Science, 1919, **50**, 443.

silicon in an electric furnace and following this by treatment with chlorine or phosgene to remove the iron.

5. Attention has been called to the refractory properties of zirconium carbide and the factors which limit its use.

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## DISCUSSION.

F. J. Tone[1]: It seems to me that the author has neglected the one thing which would have accomplished the removal of silicon, and that is adding more iron to the charge. He does not give an analysis of the ore, but I note that the silicon-iron ratio is 15:5, which would produce a 75 percent ferro-silicon. The addition of more iron would reduce the silica more easily, and form a heavy low-grade ferro-silicon, which would settle at the bottom of the charge. Any remaining in the charge could later be removed by magnetic concentration.

H. W. Gillett[2]: My impression is, that this was considered and tried, but that the fused zirconia was so viscous that the metallic globules would not settle out. This ought to be easier to work on a big scale than on a small one. The fused $ZrO_2$ is so very hard that crushing it for separation of buttons is quite a problem, while in the method used by Dr. Thompson the carbide is readily oxidized to loose, fluffy zirconia without fine crushing.

Colin G. Fink[3]: How do you prevent the formation of ferro-zirconium? Do you get any?

F. J. Toné: Yes, some zirconium is reduced and alloys with the ferro-silicon.

Colin G. Fink: After ferro-zirconium is once formed you do not readily eliminate the iron after that.

F. J. Toné: It is quite a problem, but by properly controlling the carbon and iron and other conditions very little zirconium need be reduced.

[1] President, The Carborundum Co., Niagara Falls, N. Y.
[2] U. S. Bureau of Mines, Ithaca, N. Y.
[3] Consulting Electrometallurgist, New York City.

J. G. THOMPSON (*Communicated*): As Dr. Gillett stated, the idea of removing the iron and silicon through the formation of ferro-silicon was tried, both with and without the addition of iron over and above that present in the original ore. These attempts were abandoned, since in all cases the resulting cooled charge consisted of an homogeneous fused mass of carbides showing no signs of metallic segregates. The charge never became really fluid, and it was concluded that the method was not feasible, either because the ferro-silicon was soluble in the fused melt, or because the fusion was too viscous to allow gravity segregation to occur.

Some attempts were made to remove the iron from the mixed carbides by magnetic separation. These were abandoned when it appeared that the magnetic portion consisted largely of zirconium carbide, while the non-magnetic portion still contained appreciable amounts of iron.

*A paper presented as part of a Symposium on Non-ferrous Metallurgy at the Fortieth General Meeting of the American Electrochemical Society, held at Lake Placid, in the Adirondacks, September 30, 1921, President Acheson Smith in the Chair.*

# PHYSICAL CHARACTERISTICS OF SPECIALIZED REFRACTORIES.[1]

M. L. Hartmann[2] and W. A. Koehler[3].

Abstract.

A series of tests to determine the transverse breaking strength of each of ten refractories, at 20° and 1350° C. Within this temperature range chrome brick showed the most decided drop in modulus of rupture, followed in order by bauxite, magnesia, fire clay and silica. Two bonded carborundum refractories showed an increase—indicating that a decrease in their cross-breaking strength must occur at some higher temperature than 1350° C.

[A. D. S.]

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## Part IV.—Cross Breaking Strength at 20° and 1350°C.

In the design of refractory parts for furnaces, muffles, and ovens, it is important to know the transverse breaking strength of the parts used. In cases where heat is transmitted through the refractory walls, as in muffle or semi-muffle type furnaces, a refractory material with a high transverse breaking strength is desirable, for this permits a thinner wall with its consequent better heat transmission.

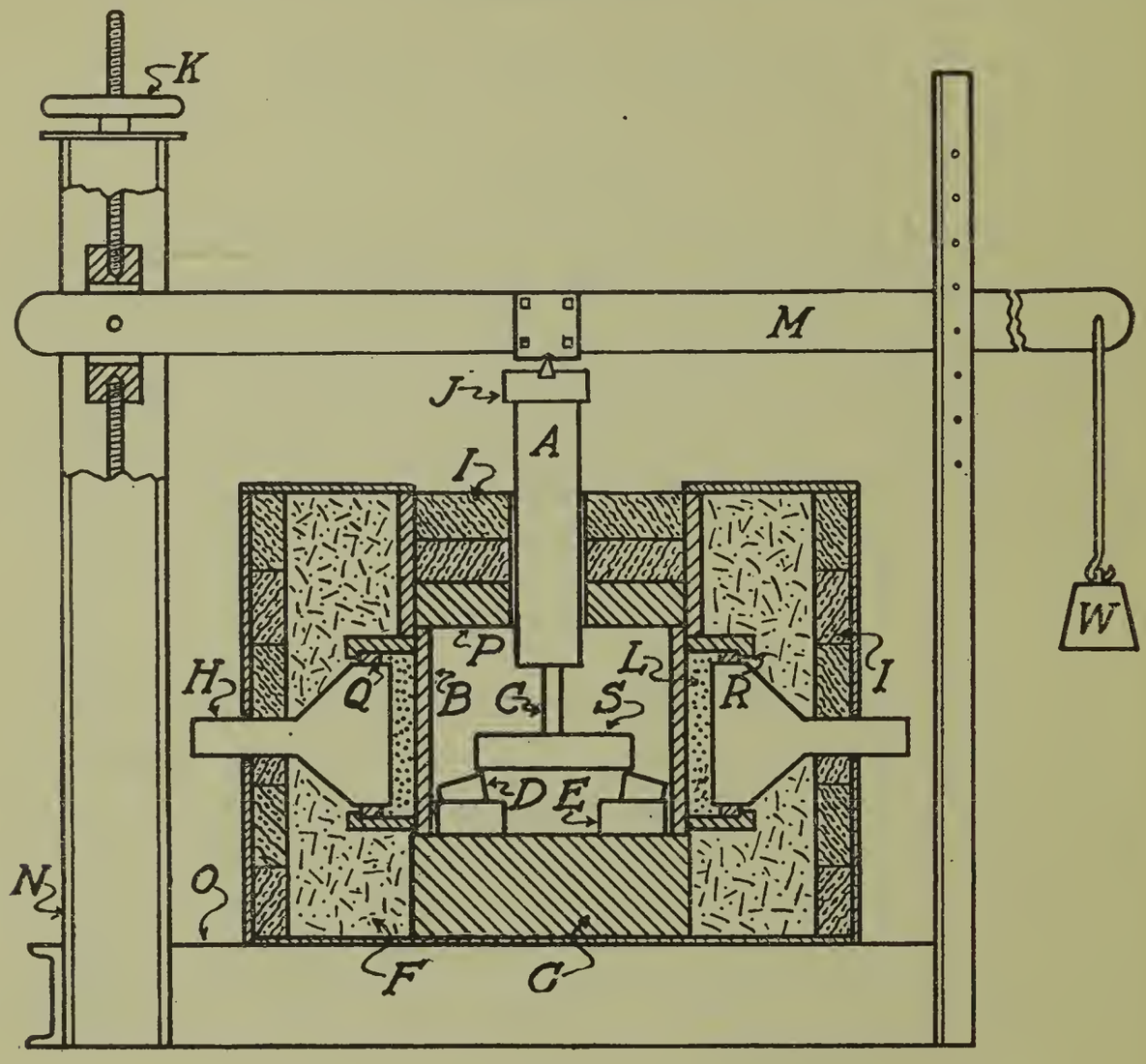
A search of the literature concerning refractories gives practically no information concerning this important physical property. S. C. Linbarger and C. F. Geiger (Jour. Amer. Cer. Soc., Vol. III, 1920, p. 543) give an account of a method of testing, but apply the method only to sagger mixes. The Bureau of Standards (Tech. News Bull., Vol. 40) reports that the transverse strength of fire clay tile at 1350° C. is practically *nil*.

[1] Manuscript received August 15, 1921. This paper is the fourth of a series on the physical properties of specialized refractories. Previous installments have been published in these Transactions, Vol. 37, p. 707-715; Vol. 37, p. 717-721; Vol. 38, p. 279.

[2] Director of Research Laboratory, The Carborundum Company, Niagara Falls, N. Y.

[3] Research Chemist, The Carborundum Company, Niagara Falls, N. Y.

This investigation is admittedly exploratory. It is obvious that an examination of many samples from all manufacturers of a given species of refractory, in an effort to secure an average transverse strength of the species, would be a long and useless investigation. We have, therefore, as in the previous papers of this series, confined our measurements to a few samples of bricks




of a given kind purchased from well known refractory manufacturers. The results, however, should serve as indication of the order of magnitude of the cross breaking strength, and this may be used to advantage in the development of new refractory materials or the improvement of the old.

## DESCRIPTION OF CRUSHING MECHANISM AND FURNACE.

The furnace consists of a shell of 10 gage sheet iron lined with two and one-half inches of insulating bricks (I) and carborundum

fire sand (F). Graphite electrodes (H) pass through the furnace walls and are in contact with the granular graphite resistor (L) which is held in place by carborundum refractory parts (B, Q, and R). The specimen (S) is supported on the edges of sections of arch bricks (D) made of recrystallized carborundum (Refrax). These are supported by carborundum bricks (E) in order to raise the specimen to the center zone of the furnace. The bricks (E) rest on a large "Refrax" block (C). The specimen (S) is ground so that it lies evenly all along the edges of the supports (D). The transverse load is applied through a thin carborundum brick (C) which is placed on the specimen midway between the supports. The pressure from the lever arm (M) is applied through the carborundum (Refrax) plunger (A). The cover (P) which also consists of carborundum refractory is covered with insulating pieces (I).

The breaking mechanism consists of two standard 6-inch channel irons (N) which are fastened to similar channels (O) used as a base. The beam (M) may be levelled (to avoid eccentric loading) by means of the hand wheel (K). The lever rests on the knife edge of the cap (J). This arrangement is similar to that described in the Am. Soc. for Testing Materials (Proc. 19, p. 581-2) for compression tests.

After the specimen has been placed in the furnace the weight of the lever (M) is removed from it by means of a counterweight and the furnace is gradually heated. The temperature is raised at the rate of ten degrees C. per minute until 1000°C. is reached, after which the rate is five degrees C. per minute to 1350 degrees C. The temperature is held at this point for twenty minutes when the weight (W) is gradually increased until the brick fails. The temperature is measured by means of a noble metal thermocouple, placed very close to the specimen under test.

The modulus of rupture R is calculated in pounds per square inch from the equation

$$R = \frac{3\,Pl}{2\,bd^2}$$

where P is the breaking load in pounds on the specimen, l is the length of the span in inches, b is the breadth in inches and d is the thickness in inches.

TABLE I.

*Cross Breaking Strength at 20°C.*

| Kind of Refractory | Apparent Density | Span Inches | Breadth Inches | Thickness Inches | | Breaking Load Pounds | Modulus of Rupture Lb. per sq. in. |
|---|---|---|---|---|---|---|---|
| | | l | b | d | $bd^2$ | P | R |
| Recrystallized Carborundum (Refrax) .... | 2.06 | 8.00 | 4.63 | 1.36 | 8.55 | 1472 | 2064 |
| | 2.18 | 8.00 | 4.64 | 1.32 | 8.07 | 1600 | 2378 |
| | 2.11 | 8.00 | 4.63 | 1.32 | 8.05 | 1672 | 2495 |
| | 2.12* | | | | | | 2312* |
| Bonded Carborundum (Carbofrax A) .. | 2.21 | 8.00 | 4.64 | 1.30 | 7.83 | 1473 | 2255 |
| | 2.27 | 8.00 | 2.40 | 2.56 | 15.70 | 2752 | 2103 |
| | 2.22 | 8.00 | 2.36 | 2.56 | 15.45 | 2510 | 1950 |
| | 2.23* | | | | | | 2103* |
| Bonded Carborundum (Carbofrax B) .. | 2.37 | 8.00 | 4.72 | 1.24 | 7.24 | 1552 | 2570 |
| | 2.35 | 8.00 | 4.75 | 1.27 | 7.65 | 1724 | 2703 |
| | 2.34 | 8.00 | 4.75 | 1.28 | 7.78 | 1740 | 2680 |
| | 2.35* | | | | | | 2651* |
| Bonded Carborundum (Carbofrax C) .. | 2.26 | 8.00 | 4.62 | 1.28 | 7.56 | 1392 | 2205 |
| | 2.26 | 8.00 | 4.61 | 1.28 | 7.55 | 1548 | 2456 |
| | 2.66 | 8.00 | 2.63 | 2.28 | 13.68 | 2260 | 1985 |
| | 2.39* | | | | | | 2215* |
| Silica No. 1 (Lime Bonded) .... | 1.63 | 8.00 | 4.40 | 2.41 | 25.5 | 1441 | 678 |
| | 1.61 | 8.00 | 4.52 | 2.40 | 26.0 | 1163 | 537 |
| | 1.62* | | | | | | 608* |

* Mean.

THE EXPERIMENTAL DATA.

The refractory pieces used were of the same grade and manufacture as in the previous papers of this series. In the case of silica, the bricks from two large manufacturers have been tested, those marked "No. 1" being the same as previously examined. In some cases standard nine-inch bricks have been tested, but in

TABLE I.

*Cross Breaking Strength at 20°C.*

| Kind of Refractory | Apparent Density | Span Inches | Breadth Inches | Thickness Inches | | Breaking Load Pounds | Modulus of Rupture Lb. per sq. in. |
|---|---|---|---|---|---|---|---|
| | | l | b | d | $bd^2$ | P | R |
| Silica No. 2 (Lime Bonded) .... | 1.53 | 8.00 | 4.32 | 2.36 | 24.0 | 664 | 332 |
| | 1.52 | 8.00 | 4.55 | 2.51 | 28.7 | 1205 | 504 |
| | 1.55 | 8.00 | 4.46 | 2.47 | 27.2 | 1445 | 638 |
| | 1.53* | | | | | | 491* |
| Magnesia ..... | 2.53 | 8.00 | 2.04 | 2.75 | 15.4 | 1324 | 1031 |
| | 2.66 | 8.00 | 2.28 | 2.75 | 17.2 | 2144 | 1498 |
| | 2.72 | 8.00 | 2.22 | 2.66 | 15.7 | 2140 | 1635 |
| | 2.64* | | | | | | 1388* |
| Fire Clay Grade "A" .. | 2.09 | 8.00 | 4.33 | 2.42 | 25.4 | 1136 | 538 |
| | 2.06 | 8.00 | 4.30 | 2.47 | 26.2 | 1610 | 736 |
| | 2.04 | 8.00 | 4.25 | 2.50 | 26.6 | 1428 | 645 |
| | 1.96 | 8.00 | 4.36 | 2.52 | 27.6 | 1716 | 743 |
| | 2.04* | | | | | | 665* |
| Bauxite ..... | 1.86 | 8.00 | 4.53 | 2.55 | 29.5 | 3092 | 1258 |
| | 1.90 | 8.00 | 3.08 | 2.58 | 20.5 | 2174 | 1271 |
| | 1.91 | 8.00 | 2.14 | 2.62 | 14.7 | 1732 | 1417 |
| | 1.89* | | | | | | 1315* |
| Chrome ..... | 2.90 | 8.00 | 4.53 | 2.69 | 32.8 | 2854 | 1042 |
| | 2.82 | 8.00 | 2.00 | 2.72 | 14.8 | 1924 | 1562 |
| | 2.81 | 8.00 | 2.58 | 2.75 | 19.5 | 2556 | 1573 |
| | 2.84* | | | | | | 1392* |

* Mean.

others "splits" and "soaps" have been used because the load required to break a full sized brick exceeded the capacity of the breaking mechanism.

The experimental data of the tests are given in Tables I and II, and the results are summarized in Table III. One is not warranted in drawing fine distinctions and interpretations from this small

## TABLE II.

*Cross Breaking Strength at 1350° C.*

| Kind of Refractory | Apparent Density | Span Inches | Breadth Inches | Thickness Inches | | Breaking Load Pounds | Modulus of Rupture Lb. per sq. in. | Breaking Temp. if other than 1350°C |
|---|---|---|---|---|---|---|---|---|
| | | l | b | d | $bd^2$ | P | R | |
| Recrystallized Carborundum (Refrax) ..... | 2.29 | 8.00 | 4.56 | 1.17 | 6.24 | 1411 | 2713 | |
| | 2.08 | 8.00 | 4.64 | 1.33 | 8.20 | 1270 | 1857 | |
| | 2.21 | 8.00 | 4.58 | 1.25 | 7.15 | 1632 | 2740 | |
| | 2.19* | | | | | | 2437* | |
| Bonded Carborundum (Carbofrax A) ..... | 2.27 | 8.00 | 4.58 | 1.30 | 7.74 | 1505 | 2332 | |
| | 2.14 | 8.00 | 4.59 | 1.34 | 8.24 | 1370 | 1999 | |
| | 2.33 | 8.00 | 4.56 | 1.27 | 7.35 | 1529 | 2492 | |
| | 2.25* | | | | | | 2274* | |
| Bonded Carborundum (Carbofrax B) ..... | 2.27 | 8.00 | 4.76 | 1.31 | 8.16 | 1985 | 2920 | |
| | 2.24 | 8.00 | 4.80 | 1.34 | 8.62 | 1442 | 2010 | |
| | 2.37 | 8.00 | 4.50 | 1.34 | 8.08 | 1542 | 2290 | |
| | 2.21 | 8.00 | 2.65 | 2.32 | 14.25 | 1538 | 1295 | |
| | 2.28* | | | | | | 2129* | |
| Bonded Carborundum (Carbofrax C) ..... | 2.18 | 8.00 | 4.58 | 1.31 | 7.86 | 1215 | 1855 | |
| | 2.34 | 8.00 | 4.60 | 1.22 | 6.85 | 1115 | 1955 | |
| | 2.12 | 8.00 | 4.63 | 1.34 | 8.32 | 1348 | 1945 | |
| | 2.21* | | | | | | 1918* | |
| Silica No. 1 (Lime Bonded). | 1.78 | 8.00 | 4.30 | 2.28 | 22.4 | 269 | 145 | |

* Mean.

amount of data, but some interesting facts are apparent. The extremely rapid decrease in the cross breaking strength as the temperature increases is not generally appreciated. Chrome bricks seem to be affected most by increase in temperature from 20° to 1350°C. in decreasing to one sixty-third of their cold breaking strength. Bauxite is one-thirteenth; magnesia, one-tenth; and fire clay, one-sixth. The carborundum refractories

TABLE II.

*Cross Breaking Strength at 1350° C.*

| Kind of Refractory | Apparent Density | Span Inches l | Breadth Inches b | Thickness Inches d | $bd^2$ | Breaking Load Pounds P | Modulus of Rupture Lb. per sq. in. R | Breaking Temp. if other than 1350°C |
|---|---|---|---|---|---|---|---|---|
| Silica No. 2 (Lime Bonded). | 1.55 | 8.00 | 4.60 | 2.52 | 29.2 | 395 | 162 | |
| | 1.52 | 8.00 | 4.63 | 2.45 | 27.8 | 447 | 193 | |
| | 1.53* | | | | | | 178* | |
| Magnesia ..... | 2.55 | 8.00 | 4.47 | 2.72 | 33.1 | 394 | 143 | |
| | 2.72 | 8.00 | 4.77 | 2.41 | 27.7 | 403 | 128 | |
| | 2.66 | 8.00 | 4.45 | 2.64 | 31.0 | 31.8 | 12† | 1300 |
| | 2.64* | | | | | | 136* | |
| Fire Clay, Grade "A" ..... | 2.07 | 8.00 | 4.34 | 2.36 | 24.2 | 226.5 | 113 | |
| | 2.00 | 8.00 | 4.35 | 2.49 | 27.0 | 32.2 | 14† | 1290 |
| | 2.05 | 8.00 | 4.34 | 2.45 | 26.1 | 31.7 | 15† | 1220 |
| | 2.04* | | | | | | 113* | |
| Bauxite ..... | 1.92 | 8.00 | 4.48 | 2.60 | 30.3 | 249 | 99 | |
| | 1.89 | 8.00 | 4.55 | 2.56 | 29.8 | 32 | 13† | 1300 |
| | 1.86 | 8.00 | 4.59 | 2.53 | 29.4 | 31 | 13† | 1140 |
| | 1.89* | | | | | | 99* | |
| Chrome ..... | 2.79 | 8.00 | 4.53 | 2.69 | 32.8 | 32.0 | 12 | |
| | 2.92 | 8.00 | 4.49 | 2.67 | 32.0 | 85.9 | 32† | 450 |
| | 2.70 | 8.00 | 4.50 | 2.74 | 33.8 | 87.5 | 31 | |
| | 2.87 | 8.00 | 4.44 | 2.71 | 32.6 | 32.1 | 12† | 1180 |
| | 2.82* | | | | | | 22* | |

* Mean.

† Not considered in average.

of the various types are distinctive in the high moduli of rupture both hot and cold, and in the fact that they maintain high values even at 1350°C. In the case of those two which actually show an increase in strength, there is undoubtedly a maximum tempera-

TABLE III.

*Summary of Average Cross Breaking Strengths.*

| | Modulus of Rupture Pounds per sq. in. 20°C. | Modulus of Rupture Pounds per sq. in. 1350°C. | Ratio $\frac{R \text{ at } 1350°C}{R \text{ at } 20°C}$ |
|---|---|---|---|
| Recrystallized Carborundum (Re-frax) | 2312 | 2437 | 1.05 |
| Bonded Carborundum (Carbofrax A) | 2103 | 2274 | 1.08 |
| Bonded Carborundum (Carbofrax B) | 2651 | 2129 | 0.805 |
| Bonded Carborundum (Carbofrax C) | 2215 | 1918 | .866 |
| Silica No. 1 | 608 | 145 | .228 |
| Silica No. 2 | 491 | 178 | .363 |
| Magnesia | 1388 | 136 | .098 |
| Fire-Clay | 665 | 113 | .170 |
| Bauxite | 1315 | 99 | .075 |
| Chrome | 1392 | 22 | .014 |

ture beyond which their cross-breaking strength decreases. Preliminary work indicates that this maximum point is between 1350° and 1500°C. for the bonded carborundum refractories, but is considerably higher for the recrystallized silicon carbide variety (Refrax). We expect to investigate this further.

There seems to be a reasonable doubt concerning the accuracy of wide extension of the dimensions as used in the calculation of modulus of rupture in brittle, non-elastic materials from the formula

$$R = \frac{3\,Pl}{2\,bd^2}$$

In other words, would one be safe in using these data obtained with an eight-inch span to a much longer span, or with widely different breadths and thicknesses? While some of our specimens of the same refractory material have been of dimensions such that the quantity $bd^2$ varied by 100 percent we cannot notice any trend in the results which would indicate that the formula is not accurate within these limits.

## DISCUSSION.

L. E. SAUNDERS[1]: I think emphasis should be placed on the sentence on page 458, "This investigation is admittedly exploratory." I have taken occasion, at previous meetings, to criticize the number of specimens taken in some of these tests, and I think again that criticism applies here. There should be a larger number of individual results before these averages are taken. In that connection I may say that there are particularly fireclay refractories having a higher modulus of rupture than is given in this paper.

F. J. TONE[2]: This is a free field; we put in two months' continuous work, comprising about sixty determinations, each taking several hours' operation of the furnace. As absolutely nothing had been previously published, we found the results useful, and believe they are well worth recording.

J. W. RICHARDS[3]: I understand that one large works in Germany is using altogether carborundum zinc retorts. I do not know whether they have been used in this country or not. I would like to ask Mr. Tone if he knows.

F. J. TONE: One of the largest works in this country is using carborundum retorts successfully.

J. W. RICHARDS: I have heard it said that whereas an ordinary retort will last a month, a carborundum retort will frequently last a year, and that they not only have additional strength, but much additional wearing power.

[1] Worcester, Mass.
[2] President, The Carborundum Co., Niagara Falls, N. Y.
[3] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

*A paper presented at the Fortieth General Meeting of the American Electrochemical Society held at Lake Placid, in the Adirondacks, October 1, 1921, President Acheson Smith in the Chair.*

# AN ELECTRIC STEAM-GENERATOR FOR LOW VOLTAGE.[1]

By F. A. Lidbury[2] and F. A. Stamps.[3]

## Abstract.

A description is given of an inexpensive form of apparatus and its method of employment for the generation of steam by means of alternating current of voltages from 100 to 500.

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Thermally, one kilowatt-hour is approximately equivalent to the heat produced by the complete combustion of 0.25 pound of coal; one kilowatt-year to somewhat more than that produced from one ton of coal.

The superior thermal efficiency of electric heating over fuel heating extends to the field of steam generation; electrically, figures of 95 percent can be readily attained, while the best coal boiler practice scarcely exceeds 70 percent, and in the average small isolated boiler plant the thermal efficiency is very much lower than this, how much lower it would require boldness to guess.

During the latter years of the war, in certain European countries possessing water-power resources, scarcity and high price of fuel led to the development and installation of apparatus of several types for the generation of steam by electric energy—first in Italy, then in Switzerland, in France and in Sweden. Short descriptions of some of these forms of apparatus have appeared in the American technical press.[4]

A moment's consideration of the figures given in the first two

[1] Manuscript received July 29, 1921.

[2] Works Manager, Oldbury Electrochemical Co., Niagara Falls, N. Y.

[3] Chemist, Phosphorus Compounds Co., Niagara Falls, N. Y.

[4] Canadian Engineer, **39**, 231, Aug. 12, 1920.
Power, **52**, 596, Oct. 12, 1920.
Power, **53**, 404, Mar. 8, 1921.
Power, **53**, 746, May 10, 1921.

paragraphs, even taking into consideration an efficiency from 50 to 75 percent superior, will show that it is extremely improbable that we shall find conditions in the United States, or in Canada, under which electric steam generation can be basically economical; nevertheless the matter is one in which many electrochemical industries, and some others, are interested, at least temporarily. A power-consuming establishment which operates its own hydro-electric installation and owing to daily or seasonal fluctuation of load has available to it at times various quantities of energy which it can generate at little or no additional cost can usually effect an appreciable saving in fuel by the utilization of this energy either for direct heating purposes or for the generation of steam. An industry which purchases blocks of firm hydro-electric power is likely to find itself similarly situated. This is particularly the case in times of severe business depression like the present, and it is therefore not surprising that even on this side of the Atlantic the subject has been receiving considerable attention in spite of the fact that it can, on the whole, be only of temporary or occasional economic interest.

It is of course the temporary nature of the problem which lends particular interest to the use of electric energy for the generation of steam, since it is obvious that the most efficient and satisfactory method of employing electric heating is the direct one of using the energy where it is required. The cost of the special devices for direct electric heating, together with the heavy investment usually necessitated by the elaborate system of transmission wiring, will however often be far too large for a temporary expedient; whereas in the case of steam generating the transmission system of piping already exists, and it is possible to install apparatus for electric generation of steam at a very low cost to meet many conditions.

It is not our intention to go into the problem of electric generation of steam in a general way; those who are interested in what has been done in Europe are referred to the papers quoted above. It should be added that it appears quite feasible to convert an ordinary tubular boiler by heat-insulating it and inserting resistance ribbon units in the tubes; we do not know, however, of any such installation in operation. The European designs re-

ferred to above appear to be all of the water-resistance type, in which steam is generated by the passage of an alternating current

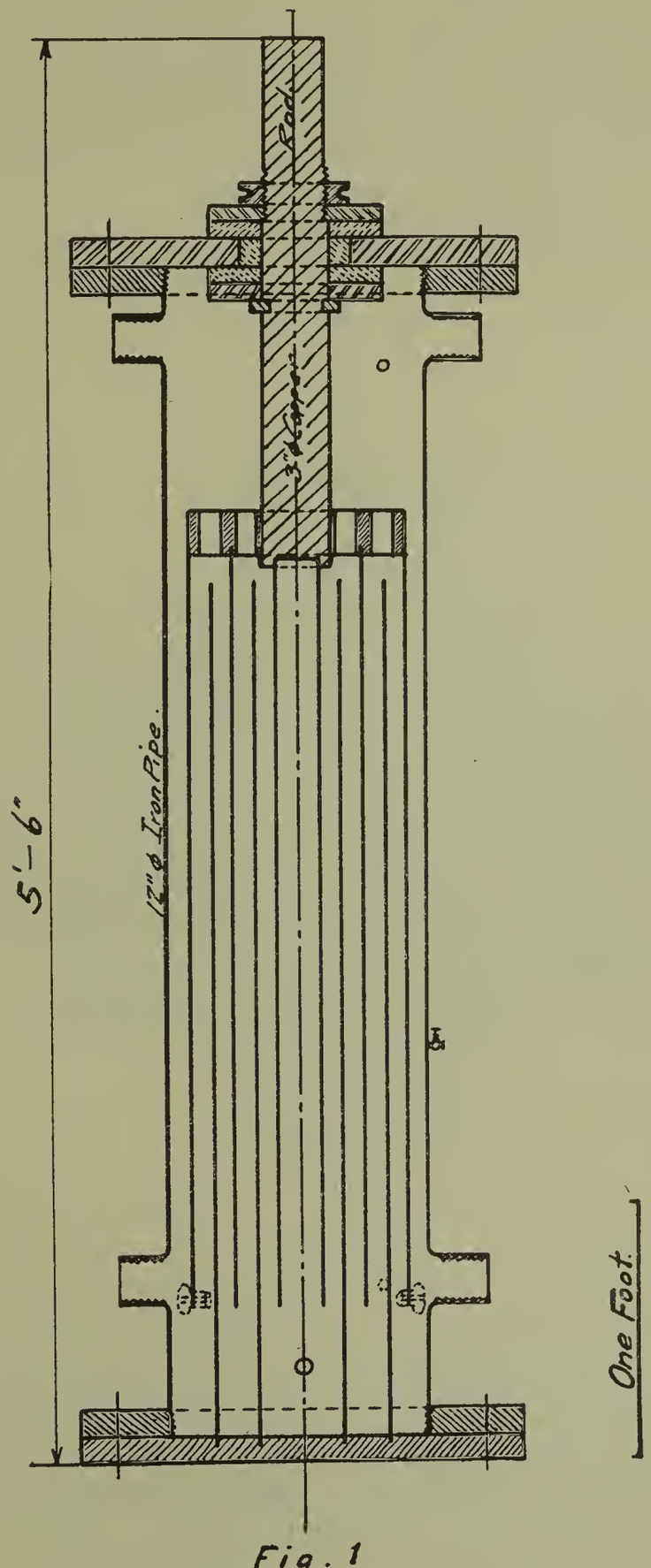


Fig. 1

through the water of the boiler itself, and are almost all for comparatively high voltage (1000 to 6000).

Figure 1 shows a section of a low-voltage electric steam-generating unit of the water-resistance type which has several well defined characteristics which make it peculiarly well adapted for use as a temporary or occasional absorber of surplus electric energy. It has been designed primarily for cheapness and simplicity of construction and compactness.

It consists of a vertical piece of 12-inch (30.5 cm.) steel pipe,

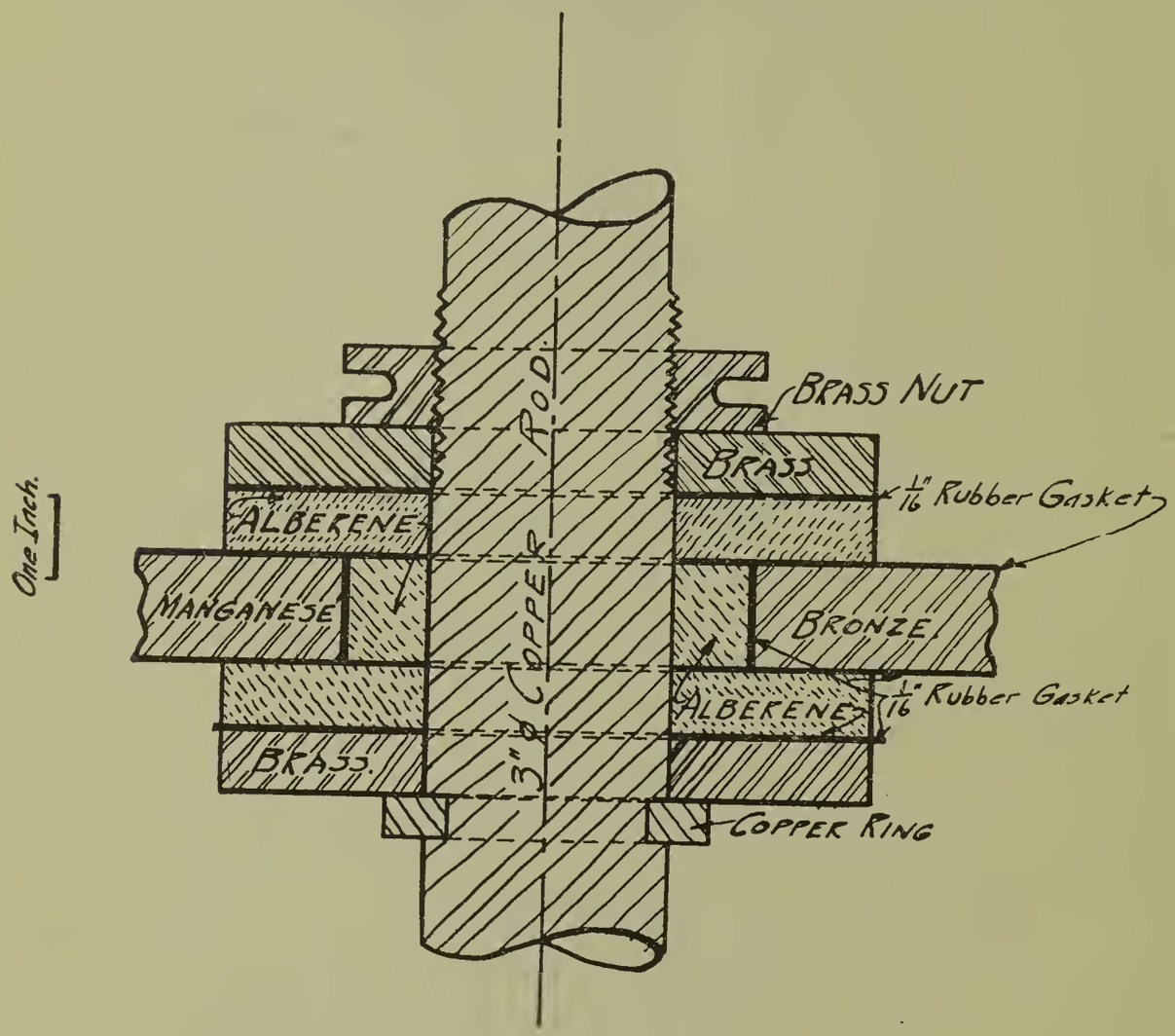


Fig. 2

fitted with steel flanges at each end, and 4.5 feet (1.37 m.) in length. The bottom is closed by a blank steel flange, which carries pieces of 8-inch (20.3 cm.) and 4-inch (10.2 cm.) steel pipe driven into concentric grooves machined in the blank flange, and the connections well soldered. These two pipes, together with the inner surface of the 12-inch (30.5 cm.) pipe, constitute one electrode. The top is closed by a flange of manganese bronze,

through a 5-inch (12.7 cm.) hole in which a 3-inch (7.6 cm.) copper rod is admitted, electrically insulated from the bronze flange by a pressure insulator, the design of which will be sufficiently clear from Figure 2. Twelve inches below the flange the copper rod terminates in a steel casting, which carries, driven on, pinned and the connections well soldered, concentric steel pipes about 36 inches (91.5 cm.) long, and of 10, 6 and 2-inch (25.4, 15.2 and 5.1 cm.) diameter respectively. These constitute the other electrode, alternating concentrically with the 12, 8 and 4-inch pipes above mentioned. The distance between opposite electrode surfaces (i.e. alternate pipes) is thus approximately 0.75 inch. The 12-inch containing tube is provided with two 2-inch outlets for steam; two 2-inch connecting tubes near the base, for use when several units are operated, for water circulation between them; and, as near as possible to the base, a 1-inch (2.54 cm.) water inlet and a 1-inch blow-off connection. There are also connections for a gauge glass near the top and bottom. The internal pipes are drilled at intervals from top to bottom, the 4-inch pipe having 12 1-inch holes, and the number increasing to 48 in the case of the 10-inch pipe; the steel casting joining the copper rod to the pipes has 18 1-inch holes. Separate electrical connections are made, in the case of the outer electrode to (a), the 12-inch shell, (b), the bottom flange, and (c), the top flange, these flanges being bolted to the flanges on the ends of the 12-inch pipe with rubber sheet packing between, and therefore requiring separate connections; the connection to the top (manganese bronze) flange serves no other purpose than to relieve the bolts, in the very improbable event of a short-circuit occurring between this flange and the inner electrode (copper rod), of the danger of heating and failing. An opening with 0.5 -inch pipe connection is provided in the 12-inch pipe about 12 inches above the bottom of the inner electrode for "bleeding", to which reference will be made later.

The apparatus as shown was designed primarily for operation at 100 volts; but there is no reason why it could not be used without much modification up to 550 volts. Its capacity at 50 pounds steam pressure is 250 K.W., and at higher steam pressures would be somewhat higher. For its operation all that is neces-

sary is to introduce water, preferably containing as much sodium carbonate as would be called for in ordinary boiler water treatment, at a rate equivalent to that at which steam is to be furnished; the rate of supply must be slower at first, until the concentration of the water in the apparatus builds up to the point at which, under the condition employed, the apparatus functions best and most smoothly; at 100 volts about 2 grams per litre, or from 40 to 50 times the concentration (as determined by titrations of chloride) of the original water supply. Once obtained, this concentration is approximately maintained by allowing the requisite quantity (1/40th to 1/50th of the amount of water supplied) to escape through the "bleeder." The concentration can however be varied within very wide limits without appreciably disturbing the smoothness of the operation, and a little experience enables one to determine, by mere observation of the height of water in the gauge glass, which will be the lower the greater the concentration, whether the "bleeder" needs to be opened or closed somewhat. In order to insure smooth operation of the bleeding valve it is necessary to cool down the water prior to its exit, and a convenient way of doing this is to run a 0.5 inch pipe through a tank containing the feed water before the valve is reached; otherwise evaporation at the valve will rapidly lead to a slowing down of the rate of "bleeding" through scaling.

Of course if the boiler be supplied entirely or largely with returned condensed water the problem of maintaining the proper concentration will be different and usually simpler, but may involve the provision of arrangements for rapidly introducing electrolyte with the water, for starting or in case of temporary loss through entrainment.

For a fluctuating load the boiler should be operated at a higher pressure than the steam main to which it is connected, and a resistance, such as a perforated diaphragm—a valve makes a very convenient adjustable resistance—interposed; also the rate of water supply should be made to correspond automatically with the load. This can be done in several ways, the most convenient of which is to supply the feed-water pipe with an automatic regulator, which will divert such water as is not required, and setting the pump to provide approximately the amount of

water required at full load. The regulator referred to consists of a sensitive by-pass valve operated by the pressure on the boiler, or rather the pressure in the feed-water pipe; as the load increases or decreases, the pressure, vice versa, decreases or increases, and the valve actuated thereby correspondingly closes or opens, decreasing or increasing the amount of water by-passed. We have been unable to find any standard type of relief valve which would operate sensitively enough for this purpose, but one can readily be made by replacing the valve of a piston-operated type of steam-pressure reducer with a balanced slide-valve, the openings of which are made V-shaped, so that the flow of water increases rapidly with the opening.

Electric steam generation naturally does not lend itself well to conditions of serious load fluctuation; in the first place the boiler cannot be forced as with fuel firing; in the second place there is practically no storage of heat in the boiler water, as this is reduced to a minimum, being little more than 1 cu. ft. in the apparatus described above. This is therefore most readily adaptable to conditions in which the surplus electrical energy available is not sufficient, and it usually will not be, to completely supplant the use of coal for steaming purposes, and in which the electrical load for steaming can therefore be kept fairly regular, and the fluctuations taken care of by the fuel-fired boilers. Much can be done, however, to adapt the apparatus to any set of conditions that may be met, as for instance by connecting it with an old boiler or similiar vessel acting as heat-storage capacity. The conditions of application can, however, vary so enormously that it would take too long to go into these possibilities; a recognition of the characteristics of the electric boiler will enable each case to be considered by itself.

A further disadvantage of the reduction in amount of water in the boiler for the sake of compactness is that if the load rapidly fluctuates the concentration of the contents of the boiler may be suddenly lowered either by boiling over through suddenly increased demand or by over-emptying through suddenly decreased demand of a more rapid nature than can be taken care of by the automatic by-pass without over-shooting through lag. To a great extent these conditions, which lead to temporary oscillations in

the load on the boiler, can be overcome, the first by the use of a steam separator to remove the solution from the steam and to return it to the boiler, the second by inserting between the water-regulating valve and the boiler a certain amount of storage capacity for the concentrated electrolyte, a convenient way of doing which would be to lengthen the boiler so as to provide more space for idle water below the upper electrodes. (In this connection it may be noted that the lower portion of the boiler, when in operation, is usually sufficiently cool to enable a hand to be placed upon it without discomfort). Much could undoubtedly be done to improve the steadiness of operation by arranging an automatic device to regulate the rate of bleeding according to the height of water in the gauge glass; but this has not yet been tried.

To anyone unaccustomed to electric steam generation, the steaming capacity of these small vessels seems remarkable. At the rated load of 250 K. W. nearly 750 pounds of steam per hour (25 boiler H. P.) are produced from unheated feed water. This rating does not represent the maximum of which the apparatus is capable; under reasonably steady conditions of load it has been frequently increased to 300 K. W. without trouble. As the limiting factor appears to be the rate at which a proper separation of steam from liquid can take place in the relatively narrow resistance paths, it is probable that by operating at voltages from 440 to 550 it could be increased considerably by halving the number of concentric internal pipes employed. At such voltages construction could also be somewhat cheapened by substituting a steel flange for the manganese bronze flange through the opening of which the current enters the apparatus; the manganese flange was adopted for fear—probably unnecessary fear—of inductive heating; and the use of bronze would certainly be unnecessary with the lower current at these higher voltages.

For the use of polyphase current, units are employed in multiple. For 3-phase current, for instance, each leg is connected to the copper rod of one vessel, and the shells, upper and lower flanges of the three vessels are electrically connected together; the voltage over each vessel being of course $1/\sqrt{3}$ of the circuit voltage.

It has already been stated that the apparatus described was

designed primarily for cheapness and compactness. A unit can be built for less than $500, or less than $2.00 per K. W., which is considerably cheaper than most electrical industrial heating appliances. It occupies little space, requires no special foundation, and can be readily moved. For the purpose of occasional or temporary energy absorption these latter qualities are of course important, as in order to save copper cost it is necessary to locate the units very close to the circuits to be used. It will usually be found possible to locate several units of such small dimensions, together with the pump and other subsidiary apparatus at almost any point indicated by the proximity of the regular circuits, particularly as the pump, etc., can be placed wherever convenient.

The efficiency at rated load is in the neighborhood of 95 per-cent. The efficiency can be determined directly by measurement of water evaporated, or, probably with more accuracy, by closing the steam valve and determining the stand-by losses involved in keeping the boiler under pressure by merely measuring the electrical in-put under these conditions. The small losses can of course be still further reduced, if it is thought worth while, by the use of heat insulation on the boiler.

Little attention is required. The writers have had a vessel of this type in operation for over six months with probably not more than half an hour's attention daily. A few minutes' attention every two hours will usually be sufficient to insure very steady running, though of course this will depend largely upon the conditions to be met and the degree to which automatic control of water supply and "bleeding" rate are carried. There would be little difficulty, even, in automatically using such an apparatus, by contact-making watt-meter control of the water supply, for the useful absorption of the valley energy of an otherwise fluctuating load curve. In ordinary running the attention required consists largely in seeing that the proper concentration range is maintained and in blowing-off accumulated sediment two or three times a day. Scale appears to form upon the pipes, but appears to fall off and to be largely removed in blowing-off. It is possible that it may prove ultimately necessary, at long intervals, to remove the top flange and internal electrodes for the purpose

of cleaning out accumulated scale; but this is not a difficult operation, and at the time of writing it is four months since the apparatus was opened for inspection.

At the time of the last inspection the active surfaces of the electrodes seemed to be showing definite signs of corrosion; what effect this will have on the durability of the apparatus is still to be determined; with the exception of the external 12-inch pipe it is not likely to lead to the necessity of frequent replacement, and the 12-inch pipe has already, as stated above, given over six months' service, is still in use, and would be a simple and cheap part to replace. It should further be added that the apparatus has run on 25-cycle current, and on the more usual 60-cycle very much less corrosion would be anticipated.

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## DISCUSSION.

L. S. THURSTON[1]: I would like to ask Mr. Lidbury where he finds most of the pitting and corrosion in the boiler, in any particular part of the tubes or any particular tube near the interior or near the exterior?

F. A. LIDBURY: Such corrosion as there is is greater near the bottom of the tubes, at the point where current is passing, irrespective of the size of the load.

J. A. SEEDE[2]: The question of utilizing electric power for steam generation has been of interest to many people. It has always appeared to me that the practice of using the water of the boiler as a resistor is one that might cause trouble, and this belief has been strengthened by noting the precautions taken by various investigators to maintain the solution strength approximately constant, by means of blow-off valves, etc. If the voltage is lowered, trouble may be expected from the electrodes or conductors, and if the voltage is increased the insulators may give trouble.

There are a number of locations in this country that offer a field for these equipments, especially paper-making plants, where large quantities of steam are used. In many plants there is the

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incentive of using excess power, especially during certain parts of the year.

With such power going to waste and coal at a high price, it is a question of simple economics to use the electric steam boiler. Instead of using the electric power to generate steam, we have approached the subject from another standpoint, that is, to build an electric preheater by passing current through the feed-water pipe, and thereby heating the water before it passes into the boiler.

Several equipments, referred to on page 468 by Mr. Lidbury, have been sold but are not yet in operation. Each consists of taking an ordinary boiler and inserting resistance units in the tubes, thus enabling an ordinary plant to be converted into an electrically heated unit at a minimum of expense.

F. A. LIDBURY: The ribbon-resistance type of boiler installation is too costly. In the first place, the units cost $5.00 to $6.00 per KW., and we actually found that to set up and insulate an old boiler for ribbon heating would cost us more than to build entirely a corresponding capacity in the water rheostat type. I am, further, afraid in the case of a scaling water, of the possible results of scale formation, since the only limit to the temperature in the tube is the rate at which the tube transmits the heat, and as the rate of transmission decreases through scaling the temperature gradient may so rise as to cause danger of burning the tube. As to Mr. Seede's impression of troubles with the water rheostat type, I have been using a low voltage boiler for a year without trouble due to the electrolyte, and Mr. Kaelin will tell you that he has been using a high voltage type without any trouble with the insulators.

F. T. KAELIN[3]: I had the good fortune of working along the same lines as Mr. Lidbury, but I had to attack the problem from the power producer's standpoint. Under the present condition of industrial depression our company was forced to find a way to use its idle power, and the best way under the circumstances looked to be the conversion of electric energy into heat energy in the form of steam. There are different types of apparatus used in Europe for producing steam electrically, but we find the simplest and cheapest apparatus is a boiler of the water

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resistance type, known in Europe as the "Revel" boiler. Three-phase current is used mainly, but a single phase can be used, of course, in the same way as Mr. Lidbury told us. This type of boiler is self-contained, requires little attention, and is quite safe in operation. Should feed water fail, power is interrupted and also the steam supply.

We started to build first one boiler of about 1000 KW., 3-phase, 2200 volts, which has now been in operation for about four months. It has worked without trouble, no scaling and very little corrosion. Corrosion depends much on the kind of electrolyte. We did not add any salt to our water, as is sometimes done. Satisfactory operation of such a boiler depends mainly on the control of the conductivity of the water forming the electrolyte. This is done by a certain amount of bleeding, which keeps the conductivity of the electrolyte constant. Our company has gone into using steam on a large scale, many conditions being favorable for such an undertaking such as close proximity of large manufacturing plants using steam for paper-making, the proper voltage available without transformation, and the simplicity and cheapness of the apparatus which produces the steam.

We have installed in a paper mill at Shawinigan Falls a three-phase boiler made up of three tanks, each one containing one electrode connected with one phase, in principle much along the same lines as Mr. Lidbury's boiler. The electric input is from 15,000 to 20,000 KW., at 6600 volts. This boiler is working at 130 lb. pressure, and produces between 45,000 and 60,000 lb. of steam an hour, which corresponds to a capacity of 1500 to 2000 boiler horsepower. This boiler is working in parallel with existing steam plant and is non-automatic, but, nevertheless, it requires very little attention.

The only regulation is done by adjusting the amount of feed water, and the amount of water discharged through a bleeder valve. The operator of the boiler can judge by the level of the water and the ammeter reading if the boiler is in proper working condition. Any change in level corresponds to the change in power input, if the conductivity of the water remains unchanged. This means the current density should never go beyond a certain limit to assure satisfactory operation.

The insulators used in this boiler, for insulating the leads connecting up to the electrodes, have to withstand considerable pressure in order to make them steam-tight. They are composed of three parts and have proved so far quite satisfactory. In Europe they use quartz. The usual boiler insurance was secured for this type of boiler.

J. W. RICHARDS[4]: During the war, when the price of coal was seventy and eighty dollars per ton in Scandinavian countries, they found it advisable to make use of their surplus electric power for heating their buildings. It was a simple operation to install one of these steam generators, by connecting it with the ordinary steam-heating supply for buildings, and even for private houses. The heating cost was, in this way, reduced to only a fraction of the cost of coal.

ACHESON SMITH[5]: Was that heating done by using the water as a resistor?

J. W. RICHARDS: I am not familiar with the apparatus.

ACHESON SMITH: Those of us who have figured on heating a boiler by means of a resistance material, have found that you get too much temperature for the amount of heat you are trying to introduce into the boiler, and you get into all sorts of expense in trying to get away from that.

CARL HERING[6]: How about drying the steam and superheating it?

F. A. LIDBURY: The steam is fairly dry; there must be a certain amount of entrainment, but in some efficiency tests we made, the efficiency obtained, (a) directly by measuring the amount of water delivered to the boiler, and (b) by taking loss figures, checked up within one percent or one and one-half percent, so that the entrainment cannot be heavy. Theoretically it would be easy to superheat, if there were any particular object to be gained, by putting in your steam line some kind of ribbon resistance, in series with the boiler, so that the current used for superheating would be proportional to the current used for boiling the water.

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